

# Advances in Polymer Coated Textiles

Edited by  
Güneri Akovali



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**A Smithers Group Company**

Shawbury, Shrewsbury, Shropshire, SY4 4NR, United Kingdom  
Telephone: +44 (0)1939 250383 Fax: +44 (0)1939 251118  
<http://www.polymer-books.com>

First Published in 2012 by

**Smithers Rapra Technology Ltd**

Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK

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ISBN: 978-1-84735-497-6 (Hardback)

978-1-84735-498-3 (Softback)

978-1-84735-499-0 (ebook)

Typeset by Argil Services

# Preface

Polymer-coated textiles are extensively used in applications such as clothing, agriculture, construction, furnishing, sports and leisure, defence and medical applications. They are in virtually every part of our daily life.

These systems are simply engineered composite materials at the macro scale. At this scale, they can offer significant improvements to the textile substrate. These improvements can be in physical properties (e.g., impermeability and fabric abrasion), and/or overall chemical properties, as well as the appearance. These improvements are dependent upon appropriately combining the advantages of the components involved.

Polymer-coated textiles are a multi-billion dollar industry. These systems employ various types of textile substrate structures available, mostly of technical textiles, which is worth  $\geq 70$  billion USD. There are several possibilities for the use of different types of polymers and textile structures as well as for their combinations. Hence, this area is open to creativity and innovative application. The polymer-coated textile industry, being parallel to developments in textile research, is very dynamic. Applications such as reactive coatings with nanoparticles (with self-cleaning, self-sterilising surfaces), systems with conductive polymer coatings to provide electromagnetic shielding (which is expected to produce  $>12$  billion USD revenue by 2015), e-(electronic) textile systems with body-monitoring properties, and environmental responsive systems are part of these exciting new developments.

This book has been prepared as an up-to-date summary of this dynamic subject by considering the passage from conventional to emerging technologies. That is, the ‘basics’ and the ‘advances’ involved in this interdisciplinary interesting area have been addressed by four experts. The basic information is given in **Chapters 1 and 2**, followed by the criteria for selection of the coat (**Chapter 3**) and textile substrate (**Chapter 4**). The manufacturing basics of the system are summarised in **Chapter 5**. Emerging technologies and applications (including smart, intelligent and nanostructured applications) are shown in **Chapters 6 and 7**, and the testing and quality-control methods of these systems discussed in **Chapters 8 and 9**. This subject cannot be covered completely and efficiently from its basic characteristics to its contemporary state in one book. Nevertheless, we hope that it will help to shed



light on the existing knowledge for textile and polymer technologists, engineers, scientists, and students.

I, on behalf of my co-authors, wish to thank Frances Powers-Gardiner (Commissioning Editor for Smithers Rapra Technology Limited, Shrewsbury, UK) for her unceasing valuable support and kind cooperation. I must also acknowledge the kind help offered by Calpreta Parkinson (Editorial and Sales Assistant) and Eleanor Garmson (Development Editor) at Smithers Rapra Technology Limited, as well as Argil Services (Typesetters).

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# 1

## Thermoplastic Polymers Used in Textile Coatings

Güneri Akovali

### 1.1 Introduction

Polymer-coated textiles are flexible composite materials comprising the coat (the polymer) and the substrate (textile layer(s)) adhered together through a specific coating process to provide additional properties for the system. A military tent can be made of a material that combines Nylon fabric with a Neoprene coat, whereas a urethane-coated polyester cloth can be used to make the inflatable chutes installed at the emergency exits on aircrafts. Other examples include protective clothing for firemen, waterproof jackets, and seat upholstery for cars. In this context, there may be two or more layers in the polymer-coated textile system, at least one of which is a textile fabric and the other is the thin continuous polymeric layer (the coat). Combination of various properties of each layer determines the overall properties of the system. That is, the textile substrate contributes to the strength (tear and tensile), elongational and dimensional properties of the system in general, whereas the polymer coat helps to introduce resistance to penetration and impermeability (to liquids, gases and dust particles), as well as improve fabric abrasion. In certain special applications, the coat can also help to increase conductivity, to provide shielding from electromagnetic interference/radiofrequency interference (EMI/RFI) and to introduce antimicrobial properties. They can also help to modify the appearance for decorative purposes.

The layers (of the textile and the coating) are bonded to each other *in situ* by the adhesive properties of the layers leading to the 'coated fabric', or by the use of an added adhesive leading to the 'laminated fabric'. In this book, the first group of systems is mainly considered.

The first step in the production of a coated textile fabric is 'direct spreading' of the (thickened liquid or paste) polymer in liquid form over the textile surface. The thickened liquid is allowed to evaporate, leaving the polymer on the fabric (if solvent-based) or allowed to transform into a coat (if plastisol- or dispersion-based); both of these processes are carried out in special ovens. During this process, appropriate

crosslinking ('curing') of the polymer coat is achieved to improve durability to abrasion and resistance to solvents (and water). This type of processing has the advantage of producing coats without mechanical or thermal stresses; however, it has the disadvantage of removal of large amounts of solvent or dispersion medium, which is energy-intensive.

The combination possibilities of the textile and coating are almost infinite, and are dependent upon final use. The polymer coat can be on one (or both) side(s) of the substrate (with identical or different types of polymers on each side), whereas the substrate can be a woven, knitted or even non-woven textile material.

Polymer-coated textiles have a very specific, important position in technical textiles and in everyday life due to their wide range of interesting applications. Some of these products are used in aerospace, automotive (e.g., airbags), chemical processing, electronic, geotextile, military, filtration and heating, venting and air conditioning applications. Other products are used in carpeting, protective clothing, fuel cells, or home furnishing applications. Examples of applications include inflatable boats, folding kayaks, gloves, snowshoes, tents and fuel tanks.

The overall properties of a polymer-coated textile are mainly dependent upon the:

- Characteristics of the textile substrate (with the exception of metallic, glass and inorganic fibre woven textiles, all other textile substrates are always polymeric).
- Characteristics of the coat applied (which is also a polymer).
- Coating/adhesion method(s) selected and employed [1] in which the adhesive used is polymeric in general.

Polymer-coated textiles can differ in material type. There are systems made from textiles of acetate/triacetate, acrylic/modacrylic, aramid, elastomeric, fluoropolymer, polyamide (PA), olefin, polyolefin, polyester, polyethylene (PE), Rayon, styrene-acrylonitrile, and polyvinyl chloride (PVC). Some coated fabrics are made of natural fibres such as cotton, wool, hemp, jute, linen (flax) or silk. Fibres of glass, fibreglass, E-glass, S-glass, rock wool, slag wool, ceramic, boron, carbon, graphite, silica, metallic fibres, and zirconia are also available.

Polymers play a dominating part in all of these systems for textiles and the coatings involved. Hence, a solid background and knowledge of polymer science and technology in addition to knowledge of textile technology and the principles of chemical engineering are prerequisites for the topic.

In the following section, a quick summary will be provided for polymers, whereas some basics of the textile substrate will be outlined in subsequent chapters.

### **1.1.1 Polymers and their Classification**

A polymer is a large molecule (polymer chain) built up by the repetition of a small, simple chemical unit ('repeat unit'), which is usually (or nearly equivalent) to the monomer, or starting material from which the polymer is formed [2].

The length (and size) of the polymer chain is characterised by its molecular weight, specified by the number of repeat units in the chain multiplied by the molecular weight of the repeat unit. To have polymers with minimum agreeable mechanical properties, it is essential to have polymers with molecular weights >10,000. This is because polymers with lower molecular weights are in the form of friable powders and cannot be put into a film. In fact, most high polymers used have molecular weights between 10,000-1,000,000.

Polymers can be synthetic (those produced synthetically (termed as being 'man-made')) or natural (produced by nature). There are >30,000 natural and synthetic polymers. Ninety percent are natural, and ~10% of them are synthetic.

Synthetic (man-made) polymers are mainly derived from petroleum, natural gas and coal as feedstocks. Annually, >150 million tons of synthetic polymers (about 20 kg per person) are produced worldwide.

Synthetic polymers can be subdivided into three main categories depending on their thermal responses:

- *Thermoplastics* consist of individual long-chain molecules that can be softened with temperature and hence are, in principle, 're-processable'.
- *Thermosets* are strong three-dimensional (3D) networks in which individual long-chain molecules are interconnected to each other by strong 'primary' covalent bonds (also termed 'chemical crosslinks'). Thermosets are usually created in the final form of the product and can be broken down only at high temperatures. They are hard and glassy at room temperature (their glass transition temperature ( $T_g$ ) values, if there are any, are much higher than ambient) and they cannot be softened by heat. Hence, they are not re-processable.
- *Rubbers* have looser 3D highly flexible networks. They are soft and elastic at room temperature. Between the chains, there are physical entanglements acting as 'physical crosslinks'.

According to these definitions (chemically) crosslinked rubbers are considered to be ‘thermosets’.

Several thermoplastics and rubbers are widely used as the coating material. Textiles applied as substrates can be prepared from natural (e.g., cotton) and/or synthetic thermoplastic polymers.

Appropriate adhesion of the textile substrate to the polymer coat is very important in almost all cases, so special polymeric adhesives are also employed.

Further key information for these three main categories of polymers is provided next.

#### ***1.1.1.1 Thermoplastics***

There are four main types of thermoplastics in common use: PE, polypropylene (PP), PVC and polystyrene. These are also referred to as ‘commodity thermoplastics’.

PE thermoplastics can be low-density (LDPE), high-density (HDPE) or linear low-density in addition to ultra high molecular weight, and medium molecular weight.

Commodity thermoplastics have low densities, ranging from 900–970 kg/m<sup>3</sup> (PE and PP) to 1400 kg/m<sup>3</sup> (PVC). This means that they have relatively low material costs per volume.

The second group of thermoplastics are engineering thermoplastics. They have better mechanical properties than commodity thermoplastics. Examples include polyethylene terephthalate, polybutylene terephthalate, PA (or Nylons), polycarbonate, polymethyl methacrylate (PMMA) and polyetheretherketone. They are characterised mainly by their strengths, with high stability performances in continuous use at temperatures >100 °C. Engineering thermoplastics are produced and used on a small scale and have prices higher than those for commodity thermoplastics.

The final group of thermoplastics is speciality plastics. They have specific properties (e.g., high heat resistance, exceptional mechanical properties). They are usually produced in limited amounts and are the most expensive. Polytetrafluoroethylene (PTFE; Teflon) is considered to be a speciality plastic with unique low-friction properties.

In terms of microstructures, thermoplastics can be amorphous glassy or a semi-crystalline solid. The amorphous thermoplastics are glassy up to a specific temperature (the  $T_g$ ), above which they transform into a more rubbery structure without a distinct

melting point. Semi-crystalline thermoplastics are two-phase materials comprising an amorphous phase with the certain  $T_g$  and a crystalline phase with a specific melting temperature ( $T_m$ ).

In general, the size of the polymer chains (which characterises the average molecular weight) and the melting points are directly inter-related up to a certain point. That is, systems with shorter chain lengths melt at relatively low temperatures; the bigger the size of the chains the higher the melting point.

There is a similar hyperbolic relationship between  $T_g$  and chain length up to a characteristic chain length. Usually, the  $T_m$  and  $T_g$  values of polymers are presented for systems with chain lengths above those ceiling values, which are characteristic of the polymer chains under consideration.

#### **1.1.1.2 Thermosets**

Almost all thermosets are hard, rigid and brittle, with high temperature and chemical resistances. They are usually used as matrices for reinforced composites. The crosslinking reaction (which occurs in the final stage of the product) is usually used to provide good adhesion with other polymers. Some thermosets such as epoxy, phenolics and polyester resins, are mainly used as the matrices for fibre-reinforced composites, whereas amino resins are mainly used for bonding chipboard.

If the number of branch points in a polymer system is progressively increased, long branched molecules with infinite 'tree molecules' are initially formed and ultimately a 3D network system is obtained. Formation of a single tree molecule (also called as the 'gel point') is when most of the polymer becomes non-soluble, and a swollen gel forms if a solvent is added to the system.

Thermosets and rubbers are examples of infinite 3D network molecules. In epoxy thermoset systems, there are two components: a prepolymer (of molecular weight ~1000–2000 with reactive epoxy groups at each end), and a multifunctional amine 'hardener'. In the crosslinking reaction, the epoxy ring is opened and linked to four others of the prepolymer chain if they are used in stoichiometric quantities. For an epoxy thermoset, the upper limit for thermal degradation is typically at 145 °C.

Other thermoset systems usually produce less well-defined networks. For example, polyester thermoset systems are produced from a partially unsaturated linear polyester (of the step-growth polymerisation product of propylene glycol, phthalic anhydride and maleic anhydride). The number of C=C double bonds in the unsaturated linear polyester (hence the degree of crosslinking and  $T_g$ ) are determined by the proportion

of maleic anhydride to phthalic anhydride used. In the curing (crosslinking) stage, these double bonds react with styrene to produce links of 1–3 styrene units.

The extent of the crosslinking reaction for thermosets increases the number of crosslinks and hence the  $T_g$ . The upper limit of the highest temperature for decomposition for any particular thermoset is characterised by the thermal resistances of the bonds involved.

### **1.1.1.3 Rubbers**

Rubbers are crosslinked amorphous polymers and their  $T_g$  is characteristically at or below 25 °C. In these systems, there are no rigid groups (such as phenyl rings) in the chain or as side groups, and no polar groups that can increase intermolecular forces.

Rubbers are dominated by commodity types, such as natural rubber (NR) and styrene-butadiene copolymer rubber, which are largely used for tyre production. In this and many other applications (e.g., conveyor belts, pressure hoses), rubber systems reinforced by fibres are used. The rubber matrix allows flexibility in bending, whereas the fabric reinforcement limits the in-plane stretching of the product. Raw rubber is known to have plastic-like deformation which behaves like an elastomer (i.e., a material that can undergo large elastic deformations which are reversible) only after crosslinking by vulcanisation.

There are also specialty rubbers which have certain properties. For example, butyl rubbers have low air permeability, nitrile rubbers have good oil resistance, and silicone rubbers have low temperature resistance.

As thermosets, rubbers are composed of molecules in 3D networks. In contrast with classical thermoset systems, for rubbers, it is more common to prepare high molecular weight polymer molecules first, and then crosslink them (only polyurethane (PU) rubbers are an exception to this rule). To facilitate (chemical) crosslinking for rubbers (which is also called vulcanisation), polymer chains with unsaturated carbon bonds are needed. If all the chains are saturated, appropriate copolymerisation with 1–2% of a monomer can introduce unsaturated groups. The original crosslinking (vulcanisation) agent for NR is a mixture of (2–3%) sulfur plus an accelerator. On heating to 140 °C, the sulfur reacts with C=C bonds on neighbouring chains to form sulfur crosslinks C-(S)-C. Typically, 15% of the crosslinks introduced are monosulfide ( $n = 1$ ), about 1.5% are disulfide, and the rest are polysulfide (with  $n > 2$ ). The polysulfide crosslinks are partially labile (they can break and reform with other broken crosslinks if the applied stresses are high, leading to permanent creep in the compressed rubber blocks),

which can be avoided by producing only monosulfide crosslinks through the use of 'efficient' vulcanisation systems.

Rubber networks are characterised by average network chain molecular weights (between the crosslinks):  $M_c$ . A  $M_c$  gram of rubber contains 1 mole of network chains (containing Avogadro's number ( $N_A$ ) of network chains). Because 1 m<sup>3</sup> of rubber has a mass of 1000 dg (where d is the density in kg/m<sup>3</sup>) and contains N network chains (where N is the density of network chains), the density of the network chain will be related to the molecular weight of the network chain by:

$$M_c / 1000 d = N_A / N \quad (1.1)$$

If the crosslinks are all connected to four network chains, then every additional crosslink increases the number of network chains by two, and so the density of crosslinks is  $N/2$ . Hence, the molecular weight of the network chain is inversely proportional to the density of crosslinks [3].

Table 1.1 summarises some of the characteristics of several polymers.

## **1.2 Polymeric Materials Commonly Used for Textiles Coating**

In addition to several types of thermoplastics (e.g., PVC/polyvinylidene chloride (PVDC), polyvinyl acetate (PVA), polyurethanes (PU), acrylics), almost all types of (natural and synthetic) rubbers are commonly used for the coating of polymer textiles.

Thermoplastics used in textile coating will be the main subject of this chapter; rubbers will be presented in the next chapter.

Most of the properties of thermoplastics are useful for coating because they can be used as hot-melt adhesives and can be welded by heat. The polymer to be selected is expected to have certain properties, in addition to appropriate molecular weights to provide the requisite mechanical properties with appropriate values of  $T_m$  and  $T_g$ .



Table 1.1 General Characteristics of Some Polymers			
Type of Polymer	Abbreviation Used	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)
<b>Thermoplastics</b>			
<i>(i) Commodity (Thermo) Plastics</i>			
Polyethylene Low Density	(LDPE)	-120	115
Polypropylene	(PP-iso)	-20	165
Polyvinylchloride	(PVC)	85	(220)*
Polyvinylidenechloride	(PVDC)	-17	(185-200) **
Polyvinylacetate	(PVA)	29	
Polystyrene	(PS)	100	(amorphous/atactic)
<i>(ii) Engineering (Thermo) Plastics</i>			
Polyethylene High Density	(HDPE)	-135	130
Polyethylene terephthalate	(PET)	69	265
Polyamide	(PA) (PA6)	50	215
Polycarbonate	(PC)	145	(295)*
Polymethyl methacrylate	(PMMA)	105	(amorphous)
Polyacrylonitrile	(PAN)	90	(*)
Liquid crystal polymer	(LCP)	-	420
<i>(iii) Speciality (Thermo) Plastics</i>			
Polytetrafluoroethylene	(PTFE, or Teflon)	20	(327)*
Polyetheretherketone	(PEEK)	145	335
Thermoplastic Polyurethane	(PU)	230	
<b>Rubbers</b>			
<i>(i) Commodity rubbers</i>			
Natural rubber (Polyisoprene)	(NR)	-73	-
(Polybutadiene)	(PBD)	< -90	-
Styrene-butadiene rubber	(SBR)	-copolymer 25/75-	-55
Polyurethane rubber	(PUR)		
<i>(ii) Speciality rubbers</i>			
Butyl rubbers (Polyisobutylene)	(BR)	-70	0
Silicone rubbers(Polydimethylsiloxane)		-125	-55
<b>Thermosets</b>			
Epoxy resins			
Phenolic resins (Phenolics)			
Polyester resins			
(*) decomposes			
(**) softening point			

The most commonly used thermoplastic polymers applied for textiles coatings are as follows:

- PVC
- PVDC
- PVA and acetate copolymers
- Acrylics
- PU
- Others

In addition, for several special applications, other thermoplastics (e.g., polyimide and PTFE) can also be used. In more sophisticated applications (e.g., those leading to inherently electrically conducting textile-coated systems), other selected polymers (e.g., polypyrrole) can also be employed.

### **1.2.1 Polyvinyl Chloride**

Polyvinyl chloride is a product of polymerisation of its monomer ‘vinyl chloride’. The latter is gaseous with strong carcinogenic properties. It has an International Agency for Research on Cancer (IARC) rating of A1, which means that it is a confirmed carcinogen in humans. (All chemicals used the in textile industry are subject to Control of Substances Hazardous to Health (COSHH) regulations, March 1994/1999, and to EC Directive 91/155/EEC). All chemicals used the in textile industry are subject to the ‘COSHH regulations’ (Control of Substances Hazardous to Health), March 1994/1999 and to EC Directive 91/155/EEC.

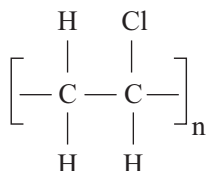
PVC and PVDC are also known as ‘vinyls’ or ‘vinyl resins’. PVC is one of the most widely used commodity polymers. It is a white, water-insoluble thermoplastic resin mainly used for coatings, insulation and piping. PVC has been used to make ‘linoleum’ for floors. In the 1970s, it was often used as vinyl tops for automobiles. It has a density of 1.38 g/cm<sup>3</sup> at 25 °C.

PVC was created accidentally by the German chemists Baumann (1872), and Katte (1912). Its potential was discovered later by the American chemist Semon (Goodrich, 1926). Patents for PVC were first taken out by Katte (until 1925), and Semon (after 1926). According to the Vinyl Institute in the USA, PVC is ‘unusual’ because it is partially (weight percentage-wise, at least) based on hydrocarbons (i.e., ethylene

obtained from natural gas or petroleum), whereas most of it is based on the salt (for chlorine). It has repeating units of  $C_2H_3Cl$  along the polymer chain.

The suspension polymerisation technique is primarily used for the production of PVC. About 20% of PVC is made by solution, bulk, and emulsion polymerisation. The products obtained from suspension polymerisation and mass polymerisations are porous and hence can absorb plasticisers easily. The products of emulsion polymerisation are non-porous fine particles. Emulsion types, only if heated to  $>80^\circ C$ , can absorb plasticisers rapidly. Emulsion-type PVC is particularly important for the preparation of coats via organo-plastisols or plastisols.

PVC (**Figure 1.1**) is a thermoplastic. It softens/fuses into a highly viscous rubbery phase if heated above the  $T_g$  and hardens if cooled below the  $T_g$ ; this cycle can be repeated many times.  $T_g$  is known as a characteristic of amorphous region properties, and it is a particularly important decisive factor for PVC for determining its thermal and mechanical properties. PVC has typical dimensional stability up to its  $T_g$  with good creep resistance, low shrinkage, good impact resistance (except notch sensitivity), and good transparency. The  $T_g$  of PVC is  $\sim 80^\circ C$  [4].



**Figure 1.1** Structural formula of PVC

PVC primarily has an amorphous structure (with crystallinity of  $\sim 10\%$ ). Being amorphous, PVC has no distinct melting point and undergoes a significant change in properties within the temperature range  $170\text{--}180^\circ C$  with decomposition at higher temperatures ( $220^\circ C$ ), with the splitting off of HCl. PVC is relatively unstable to heat and ultraviolet (UV) light, and certain stabilisers (for example salts of barium, cadmium, epoxy plasticisers, lead, or tin) are commonly used to improve its stability. Both thermal and light degradations proceed via chain reactions after being initiated by loss of a chlorine atom from the chain, and in the presence of oxygen. Both degradation reactions are accelerated in the presence of oxygen.

PVC can not be processed alone due to its rather low thermal stability and high melt viscosity; and combination with suitable additives is necessary during its pre-processing. The proper appropriate mixture with PVC and the additives (called as 'the compound') is then converted to a gelled material by heat and shearing, and is then processed. The additives used provide easy processability, as well as, giving a wide range of desired properties for different end-use applications after the processing. In fact, through appropriate formulation, a huge number of different PVC-systems can be planned and generated, which makes PVC as one of the most commonly used commodity plastics. One of these applications is in textile coating.

PVC compounds are, in generally formulated by using plasticisers (a wide variety of low or medium molecular weight chemicals, also termed as 'flexibilisers'), to yield to materials with properties ranging from rigid to soft and flexible, can be produced simply by varying the plasticiser contents, from a few percent to more than >60% percent, respectively. Plasticised PVC, is the preferred form to use in textile coating, whereas rigid PVC can be obtained from blend compounds without plasticisers, and are known as 'unplasticised PVC', or 'rigid vinyl'. Since pure PVC is hard and brittle, it must be softened properly by the use of plasticisers, for application as a coat.

Plasticisers function by lowering the  $T_g$  (if flexibility at ambient temperature is needed, lowering the  $T_g$  to below room temperature is necessitated). This can be achieved by the use of effective plasticisers (compatible chemicals with permanent features, also called 'external plasticisers') or by using appropriate copolymers to alter the main molecular structure of the main polymer chain (e.g., vinyl chloride-vinyl acetate copolymer, also called 'internal plasticisation').

External plasticisers are liquids of negligibly low volatility that are compatible with the polymer. Plasticisers are classified according to the degree of compatibility with the polymer matrix. Primary plasticisers are highly compatible with the polymer matrix and have permanent properties. Secondary plasticisers have limited compatibilities and are usually employed to introduce special properties to the system other than mechanical properties or to reduce cost.

Within primary plasticisers for PVC, there are:

- Phthalates (mainly  $C_8$ , including di-2-ethylhexyl phthalate and diisooctyl phthalate.
- Phosphates (mainly organic esters of phosphoric acids), the most important characteristic being  $T_g$  (i.e., tricresyl and trixylil, which also provides fire retardance).
- Epoxides (epoxidised soybean or linseed oil).

- Polymeric plasticisers (mostly saturated polyesters).

Secondary plasticisers include aliphatic diesters (esters of adipic, azelaic and sebacic of certain branched alcohols), which also provide low temperature flexibilities to PVC.

The liquid compositions of PVC with plasticisers are usually produced from lattices obtained from the emulsion polymerisation of vinyl chloride. These are then dispersed into plasticisers to make plastisols, or into mixtures of plasticisers and selected other organic liquids to make organosols. Plastisols are also termed 'pastes'.

In such compounds, in addition to plasticisers, there are several other additives are used. These include UV/radiation and heat stabilisers, antioxidants, fire retardant chemicals, pigments, coupling/bonding agents, colorants, blowing agents, and even fillers [5, 6]. PVC particles remain dispersed in the liquid until the mixture is subsequently heated to  $>120\text{ }^{\circ}\text{C}$ ; the mass gels and fusion occurs, yielding the solid coat with, in the case of organosols, loss of solvent.

There are several typical textile products with PVC coatings. These include: tarpaulin (which is the main outlet for PVC plastisol-coated polyester or Nylon woven fabric [7]); awnings (usually with PVC, PP or acrylic polymeric coats on Nylon, polyester or textile); tents of different sizes (in general, smaller ones are made of PU and the larger ones of PVC or Neoprene-coated polyester/Nylon woven fabrics); upholstery items (mainly transfer-coated PVC with expanded grades for a soft touch) and in protective clothing (e.g., PU transfer-coated items); 'leather cloth' materials for garments and luggage (from PVC transfer coating); and banners and bunting.

Some of the main advantages and disadvantages of using PVC as a coating are summarised next.

The advantages of using PVC as a coat are:

- PVC is a versatile, economical polymer.
- PVC has good resistance against oil, solvent and abrasion; it also has advantages with respect to heat and radio frequency weldability.
- PVC can be readily compounded with a series of different additives (including plasticisers).
- PVC has inherent good fire retardant resistance (which can be further improved).

The disadvantages of using PVC as a coat are:

- PVC tends to crack when cold.

- If PVC is prepared with plasticisers, there is the danger of plasticiser migration. This has drawn strong criticism from environmentalists when classical plasticisers (e.g., phthalates) have been employed [8], mainly because of their possible biochemical effects. Now, in almost all countries, the use of new, safer alternative plasticisers ('green plasticisers') has been enforced. In addition to plasticisers, other possible contaminants (e.g., various stabilisers and heavy metal ions) should be considered.
- PVC has moderately low heat resistance.
- PVC has low ageing resistances.

PVC-coated textiles have several architectural applications [7]. It is the most common polymeric coating material used in the production of tarpaulins and tents. Its use in upholstery ('synthetic leather') and as protective clothing are also very common.

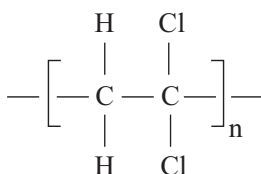
### **1.2.2 Polyvinylidene Chloride**

Along with PVC, PVDC is a member of the 'chloropolymers' family. It is a thermoplastic vinyl polymer.

PVDC is the polymerisation product of vinylidene chloride monomer (VDC) in emulsion. Its emulsions are used to impregnate mainly fabrics, leather and paper. PVDC polymer is physiologically harmless, and has repeating units of  $C_2H_2Cl_2$  along the polymer chain ( $-[CH_2-CCl_2-]$ ). It is a strong polymer with high tensile and flexural strengths. It is a white powder with a softening temperature range of 185-200 °C. PVDC is used to products with properties ranging from soft-flexible to rigid. The degree of crystallinity can be  $\leq 50\%$ , and density (at 30 °C) is  $\sim 1.87 \text{ g/cm}^3$ . PVDC is combustible but self-extinguishing, and may release HCl gas when heated.

PVDC is invented incidentally by a laboratory worker and a college student (Wiley, Dow Chemical, 1933). Its first application was by the military. They sprayed PVDC on fighter planes to guard against salty sea spray. In addition, car-makers used it for upholstery. The most popular use came in 1953, when Saran Wrap was introduced. In 2004, however, the formula was changed to LDPE out of environmental concerns about the chloride existing present in PVDC.

PVDC (Figure 1.2) is largely used as a clear, flexible and impermeable food wrap. PVDC Shrink (also called 'cling film' or 'cling wrap'), is a thin, plastic film (Saran Wrap).



**Figure 1.2** Structural formula of PDVC

The advantages of using PVDC as a coat are:

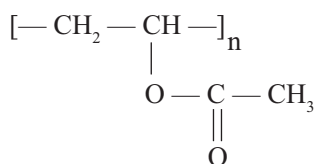
- PVDC has exceptional fire retardancy properties which can be further improved by blending it with PVC.
- PVDC has very low permeability to gases, so it is considered to be almost perfectly impermeable to gases (i.e., vapours, moisture and oxygen).
- PVDC is clear/transparent with high gloss.
- PVDC is heat-weldable.
- PVDC can be readily blended with PVC and acrylics and, because of this property, it is usually used to improve the fire retardancy of coatings.
- There is practically no effect of sunlight on PVDC.
- PVDC is resistant to strong acids and bases (except 95% sulfuric acid, as well as concentrated solutions of NaOH and NH<sub>3</sub>).
- PVDC is sensitive to electron irradiation and light.
- The thermal properties of PVDC are similar to that of PVC, therefore there are certain difficulties involved in its processing and stabilisation.

The disadvantages of using PVDC as a coat are:

- PVDC is more brittle than PVC and can easily crack if cold.
- PVDC is soluble in most organic solvents.
- The monomer, VDC, is an irritant and is genotoxic.
- Although it burns with difficulty, it burns with a green flame, producing a pungent odour and evolves the toxic gas HCl.
- PVDC can turn yellow or brown if exposed to alkalis.

### **1.2.3 Polyvinyl Acetate and Acetate Copolymers (Ethlene Vinyl Acetate)**

Polyvinyl acetate (PVAc) is the polymer of vinyl acetate; polymerisation is usually in suspension or emulsion. It is a vinyl ester, and is completely amorphous. PVAc (Figure 1.3) is used primarily in the form of emulsions, and it is also the precursor of polyvinyl alcohol and poly(vinyl acetal).



**Figure 1.3** Structural formula of PVAc

The representative polymer in this group that is widely used in textile coating is EVA polymer (polyethylene vinyl acetate copolymer). It is commonly used as a backing material for carpets and upholstery as well as the coat for wall coverings (although the polymer itself is used widely as an adhesive).

The advantages of using PVAc as a coat are:

- PVAc gives good adhesion to almost all types of polymers with very good binding properties
- PVAc is flexible at low temperatures
- PVAc is economically feasible
- PVAc is readily heat-weldable
- PVA is stable to light

The disadvantages of using PVAc as a coat are:

- The polymer is sensitive to water: it has poor wash resistance and dissolves readily in common solvents
- Over time, the polymer may show some discoloration

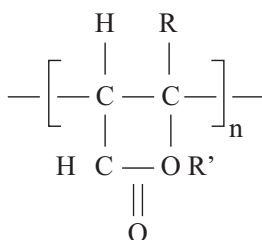


The copolymerisates of PVAc include ethylene-vinyl acetate, but they can be acrylic esters, vinyl esters or vinyl chloride. Each has different properties (e.g., the copolymerisate with vinyl chloride yields water-resistant polymers with higher hardness characteristics).

#### **1.2.4 Acrylics (Acrylic Polymers)**

Acrylic polymers are very common, and have a range of properties and prices. They are mainly used as back coatings for upholstery (fabric and carpets), as adhesives for laminates, and as lacquers for tarpaulin. The polymer itself is used as an adhesive.

The general formula for acrylics (as represented by acrylic ester) is shown in **Figure 1.4**.



**Figure 1.4** Structural formula of acrylic esters

In this group of polymers, there are mainly acrylates (where R is replaced by H in the formula shown above) and methacrylate polymers (R is replaced by CH<sub>3</sub>). In methacrylates, the most important member is PMMA, in which R and R' are CH<sub>3</sub>. The characteristics of different R and R' groups give rise to different acrylates with different properties. PMMA is made from the monomer methyl methacrylate (MMA). In general, acrylates are soft and tacky, whereas methacrylate polymers are hard and brittle.

Acrylic polymers are prepared by bulk, suspension, solution, or emulsion polymerisation. The products of the latter solution and emulsion polymerisation are preferably used for coatings. Acrylic resin coats, as waterproof coatings, are successfully applied on woven Nylon or polyester substrates with 'crushed foam coating' for curtains [9]. Modern car seats are usually back-coated with acrylics to increase abrasion resistance and to improve fire resistance.

The advantages of using acrylic polymers as a coat are:

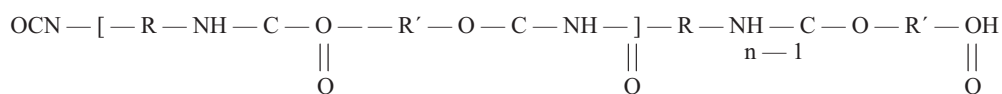
- Acrylic polymers have good clarity.
- They have high UV resistance.
- Acrylic polymers are with good resistances.
- Acrylic polymers have good resistance to ozone aging.
- They have exceptional resistance to various chemicals and water.
- Acrylic polymers can be considerably very economical.
- They can be blended with a range of other polymer types (mainly with PVC and PVDC).

The disadvantages of using acrylics as a coat are:

- The fire retardance resistance of acrylics is very poor, and acrylics have to be used by compounding with fire retardant agents.
- The monomer, MMA is toxic and, according to the IARC, is not carcinogenic [6]. MMA can exist in the bulk of the polymer as a remnant, or can also be produced from the thermal degradation of PMMA.

### **1.2.5 Polyurethane**

PU (Figure 1.5) are a family of polymers produced by the polyaddition reactions of di- or polyisocyanate with a di- or polyfunctional alcohol (polyol) [2]. They contain the (-NHCOO-) group.



**Figure 1.5** Structural formula of urethane

In the general formula of the urethane molecule presented above, variations in the R and R' groups provide several possibilities for different types of urethanes to be

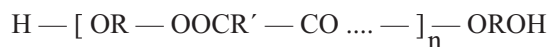
produced. Various chain extenders (such as short-chain diols or diamines) are usually employed in the synthesis of PU polymers.

*Isocyanates:* within the different types of isocyanates employed, there are aliphatic isocyanates (e.g., toluene diisocyanate, and hexamethylene diisocyanate as well as aromatic isocyanates (such as diphenyl methane diisocyanate, in addition to naphthalene 1,5-diisocyanate, xylene diisocyanate, *p*-phenylene diisocyanate and 3,3'-tolidine diisocyanate).

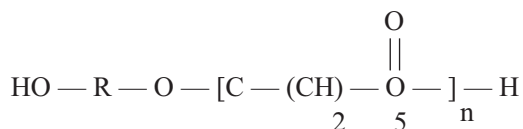
If aromatic isocyanates are used in the production of PU, the product usually rapidly becomes yellow upon exposure to the light. Hence, several aliphatic and cycloaliphatic diisocyanates (e.g., isoprene diisocyanate, cyclohexyl diisocyanate and 2,2,4-trimethyl-1,6-hexamethylene diisocyanate) are used for the production of PU. The PU become much more light-resistant and are extensively used for coatings.

*Polyols* (polyfunctional alcohols) are the second important component in the structure of PU.

There are mainly two types of polyols used: polyester (or polyether) polyols, with at least two hydroxyl groups in a polyester (or in a polyether chain), are used. Polyester polyols are saturated dicarboxylic esters (see **Figures 1.6 and 1.7**).



**Figure 1.6** Polyester polyol

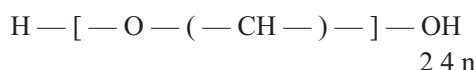


**Figure 1.7** Caprolactone polyester

Polyether polyols are polyalkylene glycols (or polyalkylene oxides) (see **Figures 1.8 and 1.9**).



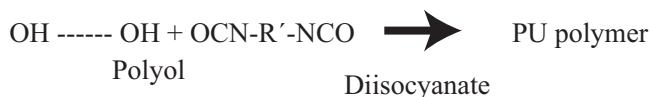
**Figure 1.8** Polypropylene glycol



**Figure 1.9** Polytetramethylene glycol

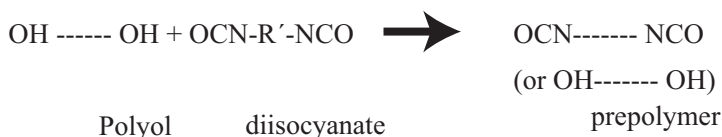
PU are prepared mainly by one of two methods: the ‘one-shot’ or ‘prepolymer’ process.

- (i) In the one-shot method, the polyol, diisocyanate, chain extender and catalyst(s) are mixed together simultaneously and PU is produced with an exothermic reaction (**Figure 1.10**).



**Figure 1.10** The one-shot process in PU production

- (ii) The prepolymer process occurs in two steps. In the first step, diisocyanate and polyol are used to produce an intermediate polymer (a prepolymer) of low molecular weight. This is then reacted with a chain extender (polyfunctional alcohol or amine) to form the final PU product with sufficiently high molecular weight in the second step (**Figure 1.11**).



This first step is succeeded by the following second step:



**Figure 1.11** Prepolymer (two-step) process in PU production

Most PU prepared have a segmented (block copolymer) structure composed of alternating ‘soft segments’ of polyol and ‘hard segments’ produced by the reaction of diol/diamine/diisocyanate. This gives rise to a heterodisperse two-phase structure of dispersed discrete hard-segment domains in a matrix of soft segments. Aggregated dispersed hard segments help to tie the polymeric chains acting as physical (virtual) crosslinks and reinforce the chains in the soft matrix. These linear PU systems are elastomeric because of this structure; the physical crosslinks due to the hard-segment domains help to provide elasticity, in addition to the soft matrix with  $T_g$  values lower than ambient temperature. They also have thermoplastic properties, being reversible to heat and solvation, both of which are important for thermoforming and solution applications. These linear PU with physical crosslinks are also called as ‘thermoplastic urethanes’ (TPU).

In TPU systems, the matrix is usually amorphous, whereas hard segments are paracrystalline or crystalline. PU systems with chemically introduced crosslinks (with chemical crosslinks, thermoset PU) may have similar morphological structures.

PU coatings of polyurethane have very good resistance to abrasion and solvent attack, and have good flexibilities and impact resistances. PU coatings are mainly prepared by conventional solution-based techniques, which use one- or two-component systems. They can be applied by dip, spray or brush techniques and adhere very well to various materials. In addition, there is the ‘hot melt’ process, which is solvent-free [10].

*The one-component system* can be a reactive one component system (using low molecular weight prepolymers with terminal isocyanate groups dissolved in low polar solvents applied as a coat directly, with water at ambient temperature acting as a chain extender and crosslinking agent) or a completely reacted one component

system (where high molecular weight PU is dissolved in a highly polar liquid (e.g., dimethyl formamide) and dried by physical means).

*For two-component systems*, a solution of the polyisocyanate component (with isocyanate-terminated prepolymers or polyfunctional isocyanates) is mixed with a polyhydroxy component to prepare the material, which is then applied as the coat.

For ‘green coating’ purposes, aqueous dispersions PU are also employed, in which lattices composed of PU-urea elastomers are dispersed in water with the aid of appropriate emulsifiers.

PU coatings are specifically preferred if unusual impact and abrasion resistances are required (e.g., floors in public buildings), as well as for various outdoor and marine uses (due to their good weatherability). PU coatings are used to produce tents of different sizes (in general, smaller ones of PU and the larger ones of PVC or Neoprene coated polyester/Nylon woven fabrics), in upholstery (mainly transfer coated PU with expanded grades for a soft touch) and in waterproof protective clothing (i.e., mainly with PU transfer coated items). Other examples include luggage, footwear, glove and waterproof mattress covers, as well as imitation leather and suede from coagulated PU [11, 12].

In brief, the advantages and disadvantages of using PU coatings on textiles or on any substrates are listed next.

The advantages of using PU as a coat are:

- PU coatings are extremely tough with very high tensile/tear/impact resistance and very good abrasion resistance.
- Their weatherabilities are very good.
- They are flexible at low temperatures with leather-like properties.
- The property of the coat can be prepared on demand. That is, the property is dependent upon the type of polyol, the molecular weight, and the ratio of hard to soft segments used in their production.
- PU coatings can give a wide range of improved properties to the substrate, including breathable microporous characteristics.
- PU coatings can be dry-cleaned (plasticisers are not used). For TPU, no curing is needed.
- PU coatings, in general, provide good adhesion to fabric substrates, have good elongation and excellent flexibilities.

The disadvantages of using PU as a coat are:

- Polyols are considered to be relatively non-toxic. However, isocyanates are highly toxic. Hence, the PU product can show significant toxicity if any remnant of isocyanate is left within it (down to 0.02 parts per million (ppm)). If such products make contact with the skin, they may produce redness leading to blistering, even to a series of possible respiratory complications upon prolonged contact [6].
- In the case of fire, even flame-retarded grades of PU can generate toxic fumes of carbon monoxide and cyanic acid

#### ***1.2.5.1 Polyurethane Foams***

In the production of PU foams, excess isocyanate groups in the polymer chain react with water (or carboxylic acids) to produce carbon dioxide. The latter blows the foam as well as simultaneously affecting the crosslinking. PU foams can be in flexible or rigid forms, mainly depending on the nature of the polymer and the type of crosslinking produced. Their production is also a multi-step process: if a bifunctional intermediate is produced, there will be flexible foams; if a polyfunctional intermediate is used then rigid foams result.

In flexible foams, the intermediate is usually reacted with an aromatic diisocyanate (e.g., tolylene diisocyanate), and tertiary amine (or stannous soap) catalysts are used, leading to crosslinks with urea linkages. This process is also suitable for one-shot processing.

#### ***1.2.5.2 Polytetrafluoroethylene Coatings***

PTFE coatings are already existing since years in a number of have been used in architectural applications (e.g., the Millenium Dome, London, UK is constructed from PTFE-coated glass fibre fabric with an estimated life time of 25 years as a 'permanent structure', [9]) and various other coated textile structures [13, 14]. Although the cost implications of using the economy with PTFE coatings do not initially seem favourable, when the performance and life times of coated textiles are considered, it they usually becomes a the preferred solution, giving rise to 'more permanent structures'. Due to the high price, its common applications are rather restricted, and are mainly used for gaskets, seals and calender belts.

PTFE is inherently fire-resistant, which is an added advantage. PTFE is inert to most chemicals and have has excellent high resistance to UV radiation, oxidation and weathering. With its unique 'non-stick' properties, it gives rise to 'mould- and

stain- free, long- term clean' surfaces. PTFE provides a quite wide service temperature ( $\leq$  up to 260 °C).

### **1.2.5.3 Polyolefin Coatings**

In this group of polymers, there are PE (LDPE and HDPE), and PP is used for textile coating. Polyolefin coatings are mainly used for tarpaulins as an alternative to PVC, for lightweight coverings, and for bulk bags and sacks of various sizes.

All three of the polymers (HDPE, LDPE and PP) have good resistance to acids, alkalis and chemicals. Their densities are small (i.e., they have a light weight for the same thickness of coat). They are low cost to use. However, their low melting points and virtually absent fire-resistance properties, in addition to limited resistances to weathering, are the main disadvantages.

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# 2 Rubbers and Elastomers Used in Textile Coatings

**Bireswar Banerjee**

## 2.1 Introduction

Rubbers and/or elastomers are the basic materials utilised for compounding in textile coating applications. They are high molecular weight, amorphous, viscoelastic polymers which have high elasticity. Rubber compounds prepared from basic natural or synthetic elastomers become soft and flow on the application of desired heat and different graduation of stress during fabric coating. In the wet process of fabric coating, a high-solid-content solution prepared in suitable solvents can also be spread at a uniform thickness on the textile substrate, and rubber-coated materials can be made.

The process of extracting natural rubber latex from the plant *Hevea brasiliensis* (a native plant of Brazil) and the procedure of using acetic acid for latex coagulation was developed by Ridley (1859–1956). This initiated the use of natural rubber in a latex or dry form for various applications. To upgrade the quality of natural rubber and its acceptability in comparison with the competition faced by synthetic rubbers, the largest natural rubber-producing country, Malaysia, had a leading role in standardising technical specifications for the production of natural rubber in the 1960s. Synthetic natural rubber, polyisoprene, was developed and had properties similar to those of natural rubber [1].

The ‘birth’ of synthetic rubbers was bequeathed to isoprene, butadiene, styrene, chloroprene, and isobutylene. These gradually invaded the market to meet the requirement of the rubber goods producing industries. There was a short supply of natural rubber during the Second World War when synthetic elastomers made inroads into the rubber-processing industries.

The use of special purpose synthetic rubbers such as polychloroprene rubber, nitrile, butyl, ethylene propylene diene monomer (EPDM) and silicone rubber have been developed and commercially manufactured by global chemical giants for use in the rubber-processing industries (including rubber-coated textiles). Various research

institutes and synthetic rubber producers are continuously researching ways to create a new generation of polymers. One example may be the development of thermoplastic elastomers. These have the processing advantages of conventional plastic and offer the end-product behaviour of rubber, and can also be used in the coating of fabrics. The manufacture of general-purpose synthetic rubber (e.g., polybutadiene) started in 1932. Special-purpose synthetic rubbers such as chloroprene rubber were commercially introduced in 1931. Butyl and silicone rubber began commercial production in 1940s, and the production of chlorosulfonated polyethylene polymers started in 1955.

In late 1963, EPDM production was introduced industrially and the commercial production of bromobutyl rubber and carboxylated nitrile rubber (XNBR) started in the early 1970s. Hydrogenated nitrile rubber (HNBR) has been produced on an industrial scale since 1988 [2, 3].

Companies wish to exploit some of the special properties of synthetic rubbers used in a wide range of textile coating applications. They are compounded exclusively from synthetic elastomers or blended with natural rubber in various proportions to obtain improved processing properties and to reduce the cost of the finished product. In some special applications, the textile - elastomer-coated product may require high weather-, chemical-, heat- and oil-resistance which can be implemented from such blending.

The most commonly used rubbers and rubbery polymers applied for textiles coatings are:

- Natural (isoprene) rubber (NR) and synthetic polyisoprene rubber
- Styrene-butadiene rubber (SBR)
- Polybutadiene rubber (PBR)
- Chloroprene rubber (CR)
- Acrylonitrile-butadiene rubber (NBR)
- Butyl rubber (polyisobutylene) (BR)
- EPDM rubber
- Silicone rubber
- Hypalon rubber (CSM)
- Polysulfide rubber
- Polyacrylic rubber
- Reclaim rubber

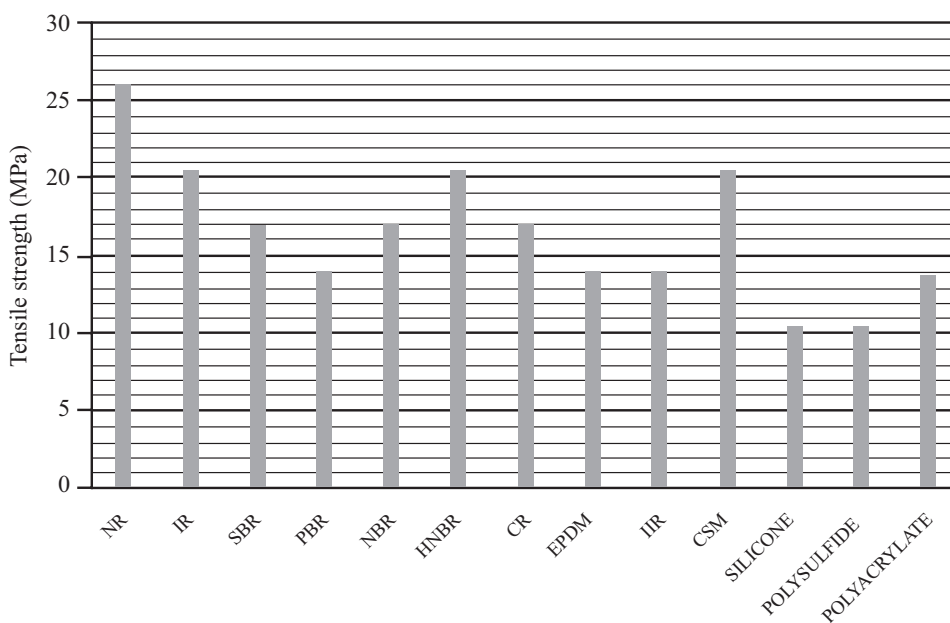
## 2.1 Natural and Synthetic Rubbers Used for the Coating of Textiles

### 2.1.1 Natural Rubber

NR is the most widely used elastomer in the textile coating industry. This elastomer has very good physical properties and processing characteristics, and excellent green tack. However, it has poor resistance to ageing and poor weatherability.

NR usually contains ~93% natural rubber (also termed ‘hydrocarbon’), plus certain inorganic salts and organic materials.

The chemical name of the NR involved is polyisoprene, polymer chains of which have the most perfect *cis*-1,4 structure, which helps to impart better mechanical properties. Its chains crystallise readily upon stretching, and hence yield at high gum tensile strengths. The inability to crystallise appropriately upon stretching generally means lower tensile strengths. Hence, appropriate reinforcing materials are required to be incorporated in those rubbers to improve the tensile strengths to approach that of NR. The tensile strengths of different rubbers are depicted in **Figure 2.1**.



Tensile Strength of various elastomers used in textile coating

**Figure 2.1** Tensile strength of various elastomers IR = isoprene rubber; IIR = Isobutylene – isoprene rubber

NR can contain several other natural resins, in addition to proteins and sugar. However, the acceptable grades of NR should always meet the acetone-soluble parameter in the range 2.5–4.5, nitrogen 0.4–0.6, and ash content 0.5–1% [1]. A general analysis of NR is detailed in **Table 2.1** [4].

<b>Table 2.1 Analysis of natural rubber</b>	
<b>Composition</b>	<b>Percentage of composition</b>
Rubber hydrocarbon	93.3
Protein	2.8
Acetone extracted matter	2.9
Ash	0.4
Moisture content	0.6

#### **2.1.1.1 Production and Processing of Natural Rubber**

Natural rubbers are produced from latex collected from the tree species of *Hevea brasiliensis*. The structure of NR is shown in **Figure 2.2**. A high grade of NR is obtained by coagulation of latex with acidification using acetic acid or formic acid under controlled conditions. The latex for light-coloured pale crepe (pale-yellow sheets) is usually strained before processing and a chemical bleaching agent (e.g., xylyl mercaptan) usually added. This is followed by coagulation of diluted latex with acids.

The preparation process starts with the collection of latex by tapping the trees of *Hevea brasiliensis*. The subsequent processes are coagulation, sheeting, drying, and baling.

During the process of producing ribbed smoked sheets before coagulation by adding acid to the latex, aluminium partitions are inserted vertically into the coagulating tanks to get the coagulum in a sheet form. The wet sheets are then pressed through a series of rolls at different speeds along with sprays of water.

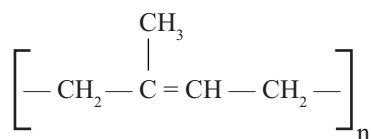
The final drying process is conducted in a smoke house or in the drying air tunnel system at 43 °C to 60 °C. The surrounding atmosphere must be free from discolouring smoke, which usually takes about 4–5 days. Dried sheets are then compressed into

bales and coated with talc powder for shipment. The final pressing of the rolls mark impressions of grooved patterns on the dried sheets. These grades of NR are the major type of elastomers used in the textile coating industry.

The dried sheets of selected pale crepes are light in colour and uniform in thickness. Colour-lightness is important for this grade of rubbers for their use in white and brightly coloured articles of coated textiles.

#### **2.1.1.2 Properties of Natural Rubber**

NR is composed of polyisoprene chains, with the *cis*-1,4 structures mentioned previously.



**Figure 2.2** Structural formula of natural rubber

*The Mooney viscosity* of commercially used NR is usually in the range 55–90 Mooney units (a larger value corresponds to a higher molecular weight of NR). This viscosity is important because during the coating of textiles (particularly in the calendering process), the success of the operation mainly depends on the viscosity and breakdown behaviour during mastication and mixing of the NR composition. Blending from different lots of rubber from the stock of this rubber usually helps in reducing this problem.

Several approaches have been made to produce technically specified rubbers such as standard Malaysian rubber (SMR), standard Indonesian rubber (SIR) and Indian standard natural rubber (ISNR).

These standards formulate the specific limit of dirt, ash, nitrogen, volatile matter and the plasticity retention index (PRI). A comprehensive specification of SMR is given in **Table 2.2** [5].

Table 2.2 Specifications for standard Malaysian natural rubber					
Property	Rubber Grades				
	CV	SMR 5	SMR 10	SMR 20	SMR 50
Dirt content (max %)	0.05	0.05	0.10	0.20	0.50
Ash content (max %)	0.60	0.60	0.75	1.00	1.50
Volatile matter (max %)	0.80	0.80	0.80	0.80	0.80
Nitrogen (max %)	0.60	0.60	0.60	0.60	0.60
Plasticity retention index	60	60	50	40	30
Mooney viscosity	60	--	--	--	--
Grade marker colour	Light blue	Light green	Brown	Red	Yellow
SMR - Standard Malaysian Rubber					

To have a constant viscosity (CV) NR of 45–55 Mooney units or 55–65 Mooney units (e.g., SMR 5 CV), treatment with hydroxylamine salts at the wet stage is usually suggested. This can give constant-viscosity grades at 45–55 Mooney units or 55–65 Mooney units.

The PRI of raw rubber is a test used to evaluate the degree of resistance to oxidation of NR. The rapid plasticity number of a sample of rubber after heating for 30 minutes at 140 °C in air indicates the ratio of the plasticity of rubber to the original plasticity, and is expressed as a number. This is expressed as a percentage of the rapid plasticity number before heating the instrument (Wallace Rapid Plastimeter). High resistance to the breakdown of rubber indicates a high PRI value but it can also indicate the presence of metallic impurities, which can lead to the oxidative degradation of NR. Furthermore, trace amounts of metals such as iron, copper and manganese may act as catalysts as aiding the oxidation of NR [3]. It can also indicate, in numerical terms, its behaviour during mastication at elevated temperatures as well as changes in property on ageing of the rubber while in use.

Superior grades of NR such as ribbed smoked sheet (RSS-1), pale crepe, and SMR 5 denotes a PRI index >70.

### **2.1.1.3 Additives Used in Natural Rubber Mixes**

Dried sheets of NR are believed to be sufficiently well-protected against oxidation. However, this protection may also be affected and reduced if there was excessive washing and heating during its processing stages. Due to the existing unsaturated character of NR chains (double bond in the main chain), the susceptibility of NR to attacks from atmospheric oxygen, ozone, and ultraviolet light are expected. Improvement is provided by the addition of suitable antioxidants into the rubber compound.

NR is not oil-resistant, and can be made to swell by several aromatic, aliphatic and halogenated hydrocarbon solvents.

Raw NR is a naturally occurring material, so it may be contaminated at different stages of production. Hence, the gradation of raw rubber must be categorised from the following parameters:

- It must be free from particles of sand and wooden bark.
- If naturally-occurring antioxidants are present in the original system, they may be removed by over-washing during preparation.
- It must be free from contamination by active metals, this may activate oxidation.
- Non-rubber constituents (if present) should be at a low, balanced level, which may even help during curing. However, as mentioned previously, over-washing of the coagulants may reduce this property.

#### **(i) Chemical Peptisers**

Market-grade NR is usually available with a high Mooney viscosity level. It is necessary to masticate the rubber to a constant viscosity before subsequent processing. To reduce its viscosity to a processable condition, mechanical mastication is necessary in a two-roll mill or in an internal mixer. To quicken the breakdown process (i.e., to facilitate mastication), a small amount of chemical peptiser such as the zinc salt of pentachlorothiophenol (trade name: Renacit-VII, Bayer) at a level of 0.2–0.5 phr are generally used. The activation process can be improved by increasing the mill temperature.

#### **(ii) Reinforcing Carbon Blacks (Fast Extrusion Furnace, Semi-reinforcing and General Purpose Furnace)**

Properties such as the gum tensile strength, flex, abrasion and tear resistance of NR are usually high. Hence, incorporation of reinforcing carbon blacks will further improve



the tensile, abrasion and tear resistance of the mixes. Graphical representation of the tensile strength of elastomers is shown in **Figure 2.1**.

In the process of calender coating, fast extrusion furnace (FEF) black provides faster calendering. Other types of furnace type black (e.g., semi-reinforcing (SRF), or general purpose furnace (GPF) can also be used in NR compounds for coating applications.

### **(iii) Metal Oxides and Silicates**

Mineral fillers which yield better dimensional stability and calendering properties for the coating are also used in compounding. These include precipitated silicas, aluminium/calcium silicates, clays, talc, calcium carbonate of precipitated and activated types (stearic acid coated for better activation), whiting, and barytes.

In combination with reinforcing carbon black, use of a certain proportion of precipitated silica can improve the adhesion to fabric substrates, and also increase the tear resistance of the compound. Reinforcing and inert white fillers are used in NR-based white or bright colour compositions for textile coating mixes.

For bright white coating compounds, titanium dioxide anatase or rutile grade is incorporated up to 20 phr to brighten the white colour; for extreme whiteness, the former type is the correct pigment. In other organic colour-base mixes, 5-7 phr of titanium dioxide may be used to obtain the appropriate shade and brightness of the colour of the mixes.

### **(iv) Process Aids**

- (1) Petroleum process oils with a 5–10 phr (or higher) level can help in the incorporation of fillers, and are particularly useful in highly loaded economic compounding for fabric coatings. They act as the plasticiser while processing to reduce the viscosity of the polymer.

Aromatic-type oils offer excellent processability for NR compounds. However, they may be for staining as well for white or coloured coatings, and can also affect the resistance to ageing. In such cases, naphthenic or paraffinic oils can be the best choice (particularly for colour mixes).

- (2) Processing aids such as brown or golden factices contribute significantly to the processing behaviour of NR compounds. Factices improve surface quality and dimensional stability in dry rubber calendering if used at 5–10 phr. They also facilitate in the dispersion of powdered fillers by controlling the ‘nerve’ (level of elastic recovery) of the elastomers.

Brown factices may cause staining in colour mixes. For white and brightly coloured compounds, use of white factices imparts similar processing results.

- (3) There is a tendency of ‘sticking to calender rolls’ for NR-based soft compounds. To control this problem, fatty acids and their derivatives (e.g., zinc salt of high molecular weight unsaturated fatty acids such as Aktiplast, Rhein-Chemie) or low molecular weight polyethylenes are employed as additives.

**(v) Antioxidants/Antidegradants**

Antioxidants/antidegradants of staining or non-staining varieties are selected for compounding NR for coating. This is achieved by considering the severity and type of service-exposure conditions (heat, ultraviolet [UV] light, flex, oxygen, and ozone).

In the low-staining antioxidant group, polymerised trimethyl dihydroquinoline (TMQ) is widely used in fabric-coating mixes.

The non-staining group of antioxidants consist of styrenated phenols (e.g., Permanax SP, Anchor Chemical) and mercapto benzimidazole (Antioxidant MB, Bayer) or phenol-alkanes (Wingstay L, Bayer) are used when extreme whiteness of the coating is desired.

Antiozonants are mostly staining (e.g., Diphenyl-*p*-phenylene-diamine, Monsanto) and they offer excellent protection in ozone-sensitive applications, and also work as an anti-flex cracking agent.

For the white/coloured NR-based coating mixes, microcrystalline waxes (e.g., MC wax, trade name: Antilux) exhibit satisfactory results if high flex is the requirement. Unlike paraffin wax, this wax does not crack if bloomed to the surface during flex, but it leaves a protective antiozonant coating.

**(vi) Accelerators**

In NR-based compounds, organic accelerators along with the activators (zinc oxide and stearic acids) are used during sulfur vulcanisation systems. Usually, for fabric-coating mixes, sulfanilamide (cyclohexyl benzothiazole sulfanilamide), thiazoles [dibenzthiazyl disulfide (MBTS)] and guanidines [diphenyl guanidine (DPG)] accelerators and a booster system of thiuram or dithiocarbamates [zinc dithiocarbamates (ZDC)] are generally used for faster curing.

Due to the high ‘heat history’ of the compound and processing at higher temperatures during mixing and calendaring, the problem of ‘scorching’ or premature vulcanisation may occur. This phenomenon can also predominate in the stocks containing

high proportions of low-structure carbon black in NR (as well as in other highly unsaturated rubbers). To control this problem during processing, a small amount of retarders/prevulcanisation inhibitors such as nitrosodiphenylamine (NDPA), salicylic or benzoic acids 0.25–0.50 phr may be added to prepare a ‘scorch safe’ compound. However, addition of these chemicals may also increase the time of cure. NDPA is staining in nature, so it can be selected in black or dark-colour compounds preferably. In white/coloured compounds, retarders such as salicylic/benzoic acid may be used without any staining effects [6].

#### **(vii) Tack Aids and Tackifiers**

Stocks used for the friction-coating of fabrics in the calendering process need to be very soft and tacky so that the mixes can penetrate the interstices of the fibres to offer better adhesion with the rubber matrix. These friction-coated textiles in a unvulcanised state are converted to construct rubber hoses, conveyor belts, tyres, and in other mechanical items as a reinforcing constituent. Addition of resins such as coumarone-indene, petroleum or wood resins help to obtain the desired tack, and these resins are also an aid to the dispersion of powdered fillers.

To promote adequate building tack for fabricated products of coated textiles in the unvulcanised state, the use of pine tar (produced by the distillation of pine wood) in black compound at 3–5 phr gives a satisfactory result. This tackifier also acts as an aid in the dispersion of high carbon black mixes, and can be used at higher proportions in friction stocks for the improvement of adhesiveness [1].

#### **(viii) Solvents and Chemical Bonding Agents**

Spreading or wet-coating of NR on textiles is facilitated by swelling the mixes in hydrocarbon solvents such as toluene, solvent naphtha or trichloroethylene. A solution of the desired viscosity is prepared, and then the mixture spread on the substrate in a rubber-spreading machine. A very thin coating on lightweight fabric by spreading or by a dipping process system can be accomplished.

This process may be followed to apply a base or anchor coating on textiles to get better adherence as part of the subsequent calendering. Application of chemical bonding agents on man-made textiles to improve adhesion with the top coating can also be prepared using this process. The coating is dried in a steam-chest after applying each coat.

#### **2.1.1.4 Derivatives of Natural Rubber**

Different types of elastomers derived from NR by chemical modification may help in the processing of textile coatings, and to help maintain ultimate product quality.

There are other categories of NR; speciality materials include:

- Superior processing natural rubber (SP).
- Deproteinised natural rubber (DPNR).
- Methyl methacrylate-grafted polymers.
- Epoxidised natural rubber (ENR).
- Synthetic polyisoprene.
- Oil-extended natural rubber.
- Liquid low molecular weight rubber.

##### **(a) Superior Processing Natural Rubber**

SP is produced by coagulation with a blend of 20% vulcanised latex and 80% unvulcanised rubber. It is blended at the latex stage and dried in the normal process. These grades of NR are used as processing aids of the compound. They help in the retention of shape, and uniform gauge thickness of the calendered articles of coated textiles by minimising the swelling and shrinkage problem that occurs immediately after calendering.

The commercial grades available are PA80 (a mixture of 80% vulcanised and 20% unvulcanised latex) and grade PA57 (with 57% vulcanised rubber plus 30 parts of process oil of the non-staining variety).

These rubbers are useful for blending with natural or synthetic rubber stocks as an aid to offer superior processing properties such as a faster calendering rate, better dimensional stability for calendered sheets, less swelling, reduced porosity of the sheeting, and improved surface finish. They are particularly useful if high percentages of elastomers are used in the mix.

SP also help in the reduction of water markings on coated fabrics that may occur during open-steam vulcanisation [5].

### **(b) Deproteinised Natural Rubber**

DPNR is produced from latex treated with enzymes to reduce or eliminate the protein content of the latex. DPNR is a highly purified form of NR with very low non-rubber constituents. It is usually available in a viscosity-stabilised form. DPNR can be used in a formulation in which the coated material comes in close contact with the skin. It can be safely used in medical applications such as non-allergic products because of the extremely low level or absence of protein in this rubber. In some cases, it has been reported that the presence of protein in NR may cause protein allergy [7].

### **(c) Methacrylate-graft Rubbers**

Methacrylate-graft (MG) rubbers can be prepared by the polymerisation of 30–50 parts of methyl methacrylate monomer in the NR latex before its coagulation. Thus, the methyl methacrylate side chains are attached on the linear NR backbone. The latex is then coagulated and crepes are produced.

MG rubbers are self-reinforcing (trade name, Heveaplus MG) and may be blended with natural and synthetic rubbers used for coating. This offers a high degree of hardness without adding any fillers to the compound, but the viscosity of the compound can be readily controlled at processing temperatures. MG rubbers can also impart stiffness and rigidity, and increase in impact resistance when used in coating mixes.

The uses of Heveaplus MG in adhesives are predominant. Its suitability of adherence to different textile substrate surfaces is the special property of this polymer when the dry compound is made.

### **(d) Epoxidised Natural Rubber**

NR shows a higher level of mechanical properties when compared with most synthetic rubbers. However, it cannot match the properties of special-purpose synthetic rubber such as gas impermeability and resistance to oil. Epoxidation of NR results in chemical modification to form ENR. This new kind of elastomer gives improved resistance to oil and can reduce gas permeability.

ENR production is by using NR latex in a hydrogen peroxide/formic acid *in situ* route with the reaction conditions carefully controlled to avoid a secondary ring-opening reaction. The first stage is addition of a non-ionic surfactant to the NR latex so that it is stabilised against acid coagulation. Epoxidation is conducted at 60–70 °C. The latex is then neutralised before coagulation upon the application of heat. It is then washed and dried in hot air. Commercially available ENR are in two categories: ENR-25 and ENR-50 mol% [8].

### **(e) Synthetic Polyisoprene**

The most important and widely applied class of polymer that can be implemented for special coating applications is synthetic NR or synthetic polyisoprene. This elastomer is produced in the solution medium using a stereospecific catalyst. It is produced with controlled molecular weights, and with a higher percentage of rubber hydrocarbons. The synthetic polyisoprene has good inherent tack, good hot tensile strength, a high modulus and good hot tear resistance in addition to a high degree of resilience and excellent compression set values. The lower viscosity of polyisoprene may reduce the breakdown time during mixing, and also shorten the warm-up time for calendering, thus saving in power and operational costs. It has low viscosity, less nerve and less swell. Hence, it may be possible to process pure gum compound prepared from this rubber in a calender to coat thin textile fabrics. Because of its high purity, water absorption is very low (<0.1% when immersed in water for 32 days), whereas ordinary NR shows values as high as 2% under similar conditions. Therefore, speciality rubber-coated fabric products with high water resistance can be produced using synthetic polyisoprene-based compounds. Brightly coloured coatings and pure-white mixes can also be prepared from this rubber because of the absence of impurities which usually affect the colour of the coatings.

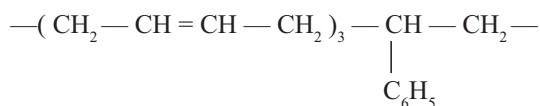
Exceptional characteristics of high purity and high gum tensile strength polyisoprene can be used in the coating of textiles, the product of which are used for medical, pharmaceutical, food-processing, and sports-goods applications [5].

### **2.1.2 Styrene Butadiene Rubber**

Styrene butadiene rubber SBR is a general-purpose, non-oil-resistant synthetic copolymer of styrene and butadiene. It can be produced by solution and emulsion polymerisation. The monomers styrene and butadiene are present in the SBR at a weight ratio of 30 (styrene) and 70 (butadiene). Polymerisation is conducted in 'cold' or 'hot' processes. Cold SBR polymerisation is carried out at 4 °C, whereas hot SBR polymerisation is at 42 °C [9].

#### **2.1.2.1 Properties of Styrene Butadiene Rubber and Textile Coating**

SBR molecules are composed of styrene-*co*-butadiene chains. The molecular structure is shown in **Figure 2.3**.



**Figure 2.3** Repeat unit of SBR

The double bond available in the butadiene molecule can be present as *cis*-1,4, *trans*-1,4 or vinyl-1,2.

Many grades of SBR are available commercially, but few types are suitable for the industry to use as textile coating compounds.

As per the norms of the International Institute of Synthetic Rubber Producers, hot polymerised, non-pigmented SBR is categorised as 1000 series, and the cold polymerised non-pigmented SBR as 1500 series. An ideal specification of SBR grade 1502 is shown in **Table 2.3** [1].

Table 2.3 Specification of SBR, Grade - 1502*	
Property	Maximum Percentage
Butadiene	75.00
Styrene	25.00
Organic Acid	7.00
Soap	0.50
Non-staining Antioxidant	1.75
Volatile Matter	0.75
Ash	1.50
Mooney Viscosity	58

\* SBR 1502 is cold grade, non-staining and non-discolouring. On proper reinforcement, this grade can give good abrasion and flex resistance properties.

The correct grade of SBR for textile coating is usually 1500 grade. This grade is also easy to blend with natural and other synthetic elastomers. This grade does not require pre-mastication during mixing, offers good dimensional stability as well as good processability during calendering, but has poor physical properties. Improvement in physical properties (e.g., higher tensile strengths and higher abrasion resistances) can be achieved if it is appropriately formulated with reinforcing fillers (e.g., carbon black and silica). In general, hot-polymerised SBR grades are difficult to process. However, they offer low shrinkage and good calendering but have poor physical properties.

The processing characteristics of SBR-based compounds are similar to that of NR. Because of its poor green tack, it is not usually used alone for coating purposes as a base polymer [2].

To improve the adhesion of SBR with the substrate, incorporation of coumarone resins in the mixes is usually done. This helps to increase the tack and physical properties of the coating compound.

Blending with NR (in the NR/SBR ratios 80:20 or 60:40) is undertaken to improve the processing characteristics of the stocks, and to get an appropriate balance of properties. This blend is also beneficial to get a better and smooth-surface finish of calendered fabric-coated items.

To maintain the uniformity of thickness across SBR calender sheeting while coating textiles using this elastomer, it is necessary for more crowns on the calender roll (0.025–0.05 mm) than the usual in relation with the roll diameter (especially if gum compound is processed).

If an exclusive SBR coating is necessary on the fabric by calendering, a thin layer of NR solution coating is required to be spread on the fabric as a foundation coating to achieve better adhesion.

SBR stocks have a lesser tendency to scorch during processing because of their low unsaturation in the polymer chain, as well as a slower curing rate than for NR. Their low unsaturation denotes better heat ageing and better heat-resistance. The elastomers also have better abrasion properties and better crack initiation resistance compared with those for NR. These rubbers show low water absorption and low ash content, and tend to maintain good electrical properties as well to high water-resistance coating.

Higher-viscosity SBR have better green strength than the low Mooney-viscosity variety and have lower porosity in cured material. They also accept higher amounts of filler loading and oil, which may be beneficial to produce low-cost coated products [4].



### **2.1.2.2 High Styrene Resins**

High styrene resins (HSR) is a copolymer which is manufactured by the emulsion polymerisation process using the same monomers and by employing a similar technology as that used for producing SBR. In this resin, butadiene content is reduced to 15% and styrene content increased to 85%. The polymer is coagulated on polymerisation and filtered. It is available in the form of thermoplastic, free-flowing, white-coloured granules.

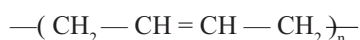
HSR is not used alone for coating applications. It is mostly used as a processing aid and in reinforcing natural and synthetic rubbers so as to increase hardness, modulus, abrasion, tear resistance, and flexibility. It can give high waterproof properties of the coating if required at a low specific gravity level. This polymer is compatible with NR, SBR, PBR, CR, nitrile, butyl and EPDM rubbers. Good colour stability and white-coloured mixes with non-staining coating properties may be achieved by including 5–10 phr of HSR in the formulation of the mixes. To get optimum results, the resin must be thoroughly blended with the basic elastomer.

Because of its thermoplastic nature, HSR begins to soften ~50 °C. However, the mixing temperature should be maintained at ~80 °C to achieve a better result of blending with the basic polymer. Incorporation of this polymer with the base rubber compounding used for coatings substantially improves the processing behaviour in mixing and calendering, as well as improving the surface finish and dimensional stability of the coated fabrics [10].

### **2.1.3 Polybutadiene Rubber**

Commercially available PBR are manufactured in a solution polymerisation system with the aid of complex organometallic catalysts.

The general formula of the polybutadiene repeat unit is shown in **Figure 2.4**.



**Figure 2.4** Repeat unit of polybutadiene rubber

Two types of solution-polymerised polybutadienes have emerged as important commercial rubbers:

- High *cis*-polybutadiene (1,4 polybutadienes).
- Medium *cis*-1,4 polybutadiene.

In coating applications, PBR is not used alone as the base polymer because of its poor gum strength and building tack. Its adhesion to fabric substrates can be compared with that of other diene rubbers. The addition of resins and compatible adhesion promoters into the mixes can improve tackiness. The preferred compounding ingredients, processing aids, and curatives are similar to those used in other general-purpose rubbers.

Blending with NR in an appropriate proportion improves adhesion, abrasion and chipping resistance if desired for severe test conditions to the fabric-coated articles. It can provide improved crack growth resistance if mixed with SBR [11].

The very high resilience, excellent low-temperature flexibility, and excellent abrasion resistance of PBR are important differences when compared with NR, SBR or EPDM polymers. The tensile strength is low, so PBR is usually blended with NR to considerably improve this property. The properties of PBR are listed in **Table 2.4**.

<b>Table 2.4 Distinctive characteristics of different elastomer used for coating</b>										
<b>Properties</b>	<b>NR</b>	<b>PBR</b>	<b>SBR</b>	<b>EPDM</b>	<b>Butyl</b>	<b>CR</b>	<b>NBR</b>	<b>CSM</b>	<b>TR</b>	<b>Silicone</b>
Adhesion to fabrics	E	G	G	F	G	E	G	G	G	E
Impermeability to air and gases	G	G	F	F	E	G	G	G	E	P
Abrasion resistance	E	E	G	G	F	E	E	G	E	F
Resilience	E	E	G	G	P	G	F	F	G	E
Environmental resistance	P	P	P	E	VG	G	P	E	VG	E
Ozone resistance	P	P	P	E	VG	G	P	E	VG	E
Resistance to UV light	P	F	F	E	G	G	F	E	VG	E
Resistance to flame	P	P	P	P	P	G	P	G	P	F
Low temp. flexibility	E	E	G	G	F	F	F	F	F	E
Electrical resistivity	E	E	E	E	E	F	F	G	G	E
Key: E – Excellent, VG – Very good, G – Good, F – Fair, P – Poor										

*Cis*-polybutadiene can maintain its resilience at  $-40^{\circ}\text{C}$ . To achieve resistance to stiffness at low temperatures, this polymer can be blended with NR and SBR stocks.

Blends with NR and SBR with polybutadiene are used to explore the unique properties of this elastomer in coated products. These include the high resilience, good crack resistance, high abrasion resistance, good ageing and weathering resistance, and overall good low-temperature flexibility of the coated matrix. PBR can also provide good dimensional stability, and improve flow properties (which are particularly important for high rubber-content compounds processed in calendering for textile coating processes).

Blends of NR/PBR in the ratio of 80:20 improve processability by contributing to increase the calender speeds at low temperature. They can also give smoother, softer, flexible, low porosity-coated articles with minimum variations in thickness.

PBR/NR-blended compounds can swell easily in hydrocarbon solvents. The prepared solution is used to spread the coating on textiles in the rubber-spreading machine (when a very thin coating or high-finish articles of the coated textiles are needed).

The rubber-based items subjected to dynamic applications (where resistance to crack initiation and growth, heat stability, low heat buildup and high wear resistance are the necessary requirements) in those areas in which PBR/NR blends are in the correct proportions will provide a long operational life. Products in these categories (e.g., conveyor and transmission belts, hoses, and inflatable items) use the rubber coating on natural/manmade fabrics to fabricate articles, which is subsequently vulcanised as a composite material.

The low water absorption of PBR is applicable to coated products such as rain jackets and snow jackets, and other high water resistance-coated items.

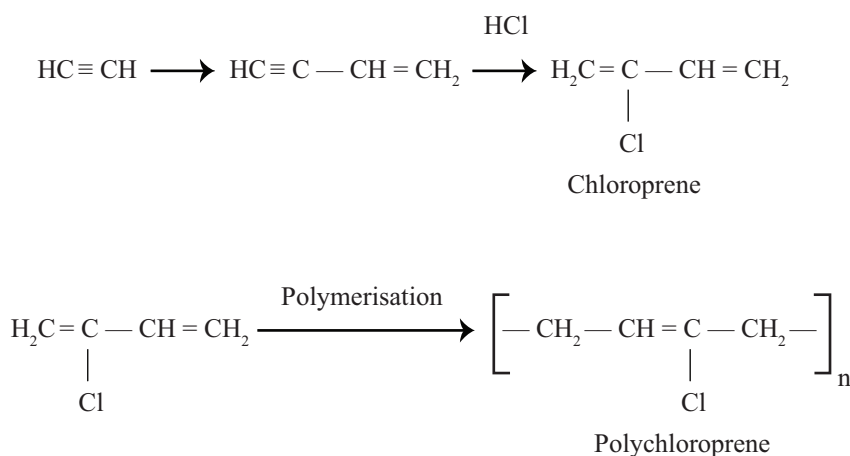
#### **2.1.4 Chloroprene Rubber**

The most common trade name of the CR polymer is Neoprene, and this term is commonly used in place of polychloroprene.

CR is manufactured by emulsion polymerisation of the monomer 2-chloro-1,3-butadiene in the presence of emulsifying agents in water, catalysts, modifiers, and protective agents. The polymerisation is conducted over a controlled period of time and temperature. During the polymerisation, mainly 1,4 addition ( $\sim 98\%$ ), and some 1,2 addition ( $\sim 1.5\%$ ) takes place. Although 1,2 additions are in a lesser amount, they should be considered with care because they usually have a pronounced effect

on the final properties of the polymer. During 1,2 additions, some chlorine is also available in the allylic form on the polymer chain, which is utilised as the curing site of the polymer. The emulsion is then coagulated and dried to obtain the polymer in a dry condition [4].

The polychloroprene polymerisation reaction beginning from the basic ingredient  $C_2H_2$  for the production of its monomer is given in **Figure 2.5**.



**Figure 2.5** Structural formula of polychloroprene rubber

Two major types of CR are used in elastomeric applications:

- General-purpose grades
- Adhesive grades

In rubber textile coating compounding, the choice of basic CR is in the general-purpose grades; the adhesive grades are applicable for making adhesives with various properties. Adhesives (which are made as room temperature-cured or high temperature-cured) are used in the fabrication of joining different materials designed and produced from CR-coated textiles.

The proofing of fabrics by spreading, calendering or laminating needs a very good building tack. Neoprene rubbers have good adhesion, similar to that for NR. However, this property can be further enhanced by adding suitable tackifiers to the compound to facilitate desired adhesion to the textile substrate.

There are many properties of CR which can be modified by blending with other rubbers. To improve elasticity and low-temperature flexibility, CR can be blended with NR. Blending with PBR may improve the brittleness point of the coating compounds at low temperatures. In the improvement of some of the mechanical properties and resistance to swelling in oils, this elastomer can be blended with nitrile rubber. To reduce the cost of the coating mixes, it is possible to blend SBR with CR, but only by taking into consideration the properties of the end-products which may have an effect due to the low gum strength of SBR.

The gum tensile strength and tear resistance of CR is high. However, further increase in these properties can be achieved by adding reinforcing carbon blacks. To get higher tear strength, reinforcing silica may be incorporated in the mixes.

Suitably compounded CR exhibits excellent ageing, weathering, and ozone resistance. It is moderately resistant to oils and several chemicals. These rubbers have good mechanical properties, abrasion resistance and very good hot air-resistance, as well as very good resilience. Their tendency to crystallisation after curing shows a high level of resistance to flex cracking, as shown in **Table 2.4**.

Non-reinforcing, non-black fillers can be added during CR-based compounding. White fillers such as calcium carbonates and silicas must be used in white or coloured compounds for coating applications. It is possible to formulate extensively long-lasting, brightly coloured coatings using this polymer. To increase the tack of the compound, tackifiers such as coumarone-indene resin and petroleum resins may be used. These tackifiers not only improve adhesion to the substrates, but also help in dispersion of the fillers in the mixes.

The particular peptising agent used for CR is piperidinium pentamethylene dithiocarbamate. This is an effective peptiser for CR that helps in the breakdown of the polymer during mixing and also promotes tack to the mixes.

In making coloured coating compounds based on CR, colours (organic or inorganic) may be incorporated into the rubber mixtures.

The white pigment titanium dioxide of rutile or anatase grades at higher amounts (up to 20 phr) can be used for white-coloured compounding, and 5–6 phr as white base if rubber colours are used for coloured mixes.

Petroleum oils and plasticisers can be added to the compounding to obtain particular properties. Plasticisers such as dibutyl phthalate (DBP), dibutyl thioglycollate (Plastikator 88, Bayer) and ether thioether (Plastikator OT, Bayer) need to be incorporated in polychloroprene-based mixes to:

- Obtain better dispersion of fillers
- Facilitate processing
- Promote adhesion

Metallic oxides such as magnesium oxides and zinc oxides are used in CR compounding. This can help in the processing safety, rate of cure, and quality of the vulcanised coating. Litharge/red lead is incorporated into the mixes to achieve improved resistance to the deterioration caused by water.

Commonly used accelerators such as sulfanamides, thiazoles, thiurams, thioureas, and sulfur are sometimes used at lower amounts as curing agents. Fast curing accelerators such as ethylene thiourea (NA 22) and di-*ortho*-tolyl guanidine are widely used in CR-based formulations.

CR have good resistance to weather and ozone, but further improvement to these properties can be achieved by adding antioxidants/antiozonants. Selection may be from generally available protective agents.

This elastomer has inherent flame retardation, which can be further improved by adding chlorinated paraffins, antimony oxides, and zinc borate into the mixes.

Crystallisation is a property of CR, and adhesive grades are more crystalline in nature. Crystallisation is time-dependent and can lead to stiffening at low temperatures. This tendency may make the coated articles unusable. Finished products after vulcanisation have fewer tendencies to crystallise than in the uncured state.

The processing behaviour of CR during mixing and calendaring is similar to that of general purpose rubbers. Caution must be exercised to eliminate the scorching tendency (particularly in the calendaring process) by reducing the 'heat history' of the compound (i.e., by controlling the mixing and warm-up mill temperature).

The calender roll temperature must be accurately controlled to improve the process of coating fabrics. A high temperature in the calender bowl may be necessary to reduce the roughness of the surface of the coated sheeting, but the compounds may stick to the calender rolls. To provide an adequate level of processing safety, rubber retarders such as nitrosodiphenylamine (Retarder J, Uniroyal Chemicals) or cyclohexylthiophthalimide (Santogard PVI, Monsanto) can be used in the mixes. A common accelerator for other rubbers, MBTS, acts as an anti-scorch agent in CR compounds.

It is necessary to use soft and sticky compounds in the friction-coating of fabrics. These can easily penetrate into the interstices of the fabrics, and improve adherence with

the top coating. These are utilised for the construction of hoses, and conveyor and flat transmission belts. To enable good friction, stock plasticisers in liberal amounts can be incorporated into the stock to develop tack and appropriate flow of the mixes. For this purpose, good peptisation of the basic rubber is also an important factor.

In the process of coating dry CR stocks by calendering (particularly if very thin coatings on lightweight fabrics are to be processed), certain difficulties may occur in obtaining a good surface finish of the coated material. To overcome this problem, a spread coating system is desirable. Suitably compounded CR can be swelled in solvents such as toluene, ethyl acetate or methyl ethyl ketone, and dough (higher solid content rubber solution) is prepared. The viscous material is then spread onto the fabric by the rubber-spreading machine, and the thickness of the coating maintained by adjusting the gap between the knife and the rubber roll.

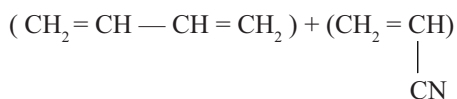
To obtain a higher thickness of coating, multiple operations can be followed by the evaporation of solvents after drying on each pass of the completed coating where the heating zone is fitted with the spreading device.

Vulcanisation of coated textiles is usually carried out in steam-heated vulcanisers in roll forms wrapped on metal drums; a festoon curing system is also employed for thin coating. Textiles of higher thicknesses can be cured using a Rotocure machine. The speed and temperature of the drums of this equipment are kept in concurrence to obtain a satisfactory and uniform curing system [6].

### **2.1.5 Acrylonitrile Butadiene Rubber (Nitrile Rubber)**

Acrylonitrile butadiene rubber is commonly known as nitrile rubber (NBR). It is the copolymer of butadiene and acrylonitrile (ACN) manufactured by an emulsion copolymerisation system. The polymerisation design and temperature are the two most important factors in the production of nitrile rubbers [6]. The structural formula of acrylonitrile butadiene rubber is shown in **Figure 2.6**.

NBR can be produced by cold or hot techniques. The cold polymerisation technique is undertaken at 5-30 °C and gives more linear polymers with less (or almost zero) gel. This elastomer can be produced by a continuous or batch process. The preferable commercial grades are made by continuous polymerisation. A manufacturing formulation of NBR is shown in **Table 2.5** [1].



Butadiene acrylonitrile



Copolymer unit

**Figure 2.6** Structural formula of acrylonitrile butadiene rubber

Table 2.5 General recipe for manufacture of NBR	
Ingredients	Percentages
Butadiene	67.0
Acrylonitrile	33.0
Catalyst	0.1
Stabiliser	1.25
Modifier	0.5
Emulsifier	3.5
Electrolytes	0.3
Activator	0.05
Short stop	0.1
Water	200.0

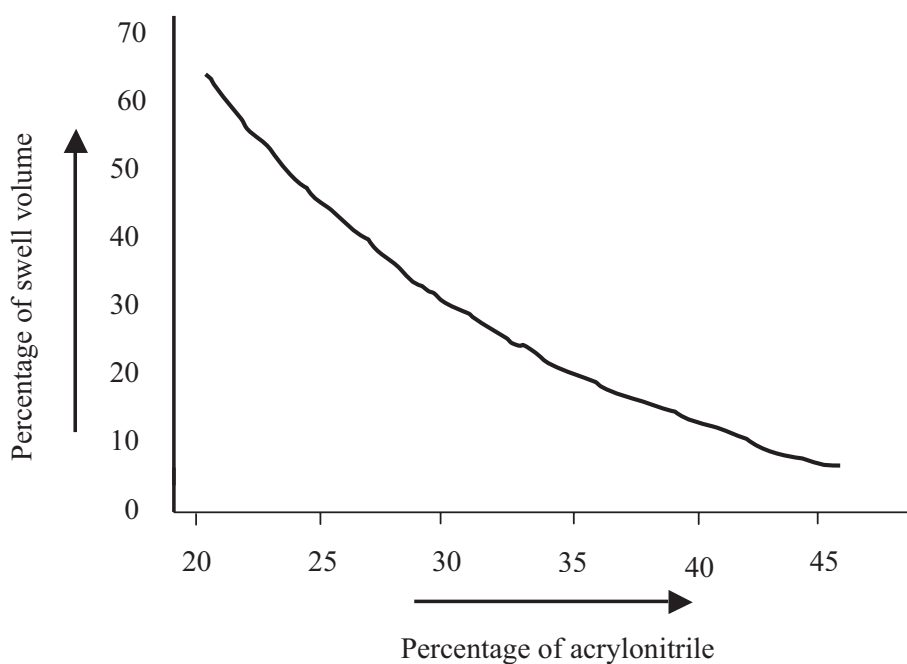
Rosin soaps or fatty acid soaps may be used as emulsifying agents of monomers in water. A short stop is added to stop the polymerisation from the latex; the monomer butadiene can be removed by lowering the pressure, and acrylonitrile is stripped in



a column with steam. Coagulation is carried out by adding salt to the latices such as NaCl or  $\text{CaCl}_2$ . After drying the crumbs, bales are made for shipment.

The hot polymerisation ( $\sim 25\text{--}50^\circ\text{C}$ ) tends to produce more sturdy structures. The reason is the presence of branching of the polymer chains during polymerisation, which is often referred to as ‘gel’. While considering the processability, ‘cold’ rubbers are always preferred because of less chain branching or gel as compared with hot grades.

The most outstanding property of NBR is its high resistance to mineral and vegetable oils, greases, and hydrocarbon liquid fuels. Different grades of these oil-resistant rubbers are commercially available based on the acrylonitrile content of the polymer, which ranges from 18% to 50%. The physical properties and processing behaviour of NBR are directly related to the proportion of acrylonitrile present in the polymer. The percentage of volume swelling in oil in relation to acrylonitrile content is shown in **Figure 2.7** [4].



**Figure 2.7** Percentages of volume swell in relation to ACN content

Higher acrylonitrile content increases properties such as oil and fuel resistance, tensile strength, and hardness, along with the following attributes:

- Improvement of resistance to abrasion
- Improvement in heat resistance
- Improvement in gas impermeability
- Reduction of resilience
- Reduction of glass transition temperature ( $T_g$ ) (i.e., at 18% acrylonitrile, the  $T_g$  is  $-38\text{ }^{\circ}\text{C}$ , and at 50% it is  $-2\text{ }^{\circ}\text{C}$ ).

Low acrylonitrile grades decrease oil resistance and tensile strengths, but improve low-temperature flexibility, resilience, elasticity, and compatibility with plasticisers (Table 2.4).

The compatibility of blending NBR with NR is not satisfactory. However, it can be suitably compounded in blending with SBR. To improve the inherently poor ozone resistance, NBR can be blended with polyvinyl chloride polymer and EPDM.

The low mechanical properties of NBR can be improved by suitable compounding with reinforcing fillers such as carbon blacks, reinforcing silicas, phenolic and epoxy-type resins. This may also increase the hardness and physical properties. The reinforced tensile strength of this elastomer is shown in Figure 2.1.

Addition of resins such as coumarone-indene and factices incorporated as processing aids in compounding improves calendering. Improvement in calendering can also be achieved by adding plasticisers and tackifiers in the compound to control the shrinkage, flow, and dimensional stability of the coated material.

Plasticisers of low molecular weight monomeric esters such as DBP and dibutyl sebacate along with tackifying resins are used in the improvement of tackiness of NBR, which is inherently low. It may also help in the dispersion of fillers and in the improvement of adhesion to textile substrates. Because of low building tack, a small proportion of well-masticated NR can help to overcome this problem.

Very low-viscosity, low molecular weight liquid NBR can be incorporated as a plasticiser, and is compatible with dry NBR-based compounds. Unlike other chemical plasticisers, this grade of liquid nitrile has very low or zero extractability, and can crosslink partially during cure to the main chain.

Inclusion of a high amount of plasticisers into the mixes may reduce swelling resistance, and can be volatilised at high service temperatures.

Friction coating on textiles using the calendering process and fabrication for the manufacture of oil-resistant belts from nitrile rubber compound is possible if the stock made is sufficiently soft to follow this technique. A very thin coating on a fabric may also be possible using this system of coating in the calender.

It is difficult to process NBR stocks in the calender for coating applications on textiles, particularly if coating of higher thicknesses is to be employed. This is because of a non-smooth surface finish, and improper adhesion with substrates.

In this case, preparation of a viscous solution of nitrile rubber compound in a suitable solvent (or blend of solvents) and application of the coating on textiles by a rubber-spreading machine can be applied. This is also good practice to obtain good surface finishes of the coated material.

To achieve a higher coating thickness, multiple layers of coating can be applied (after drying of each coat) to obtain the desired thickness. However, coatings produced by spreading are expensive because of the high cost of solvents.

Suitable solvents for the preparation of spreading dough are usually polar solvents such as acetone, methyl ethyl ketone, toluene and xylene.

NBR is susceptible to ozone attack. Protection against ozone is necessary by adding antiozonants to the mixes if this property is required to be improved to match the service conditions. Selection of the appropriate accelerators, antioxidants, and antiozonants for nitrile rubber compounds is from commonly used chemicals available in the general rubber-processing industry, and gives satisfactory results.

The choice of curing agent is dependent upon the processing safety while coating in a calender, and also on the heat history of the compound. Nitrile rubbers can be cured by sulfur, but the solubility of sulfur is much lower in this type of rubber. Hence, magnesium carbonate-coated sulfur is employed, and the sulfur is added at the early stage of the mixing cycle to obtain better dispersions.

The products of nitrile rubber-coated items include oil-resistant conveyor belts, hoses, textile aprons and cots, collapsible fuel tanks, blankets for offset and photogravure printing, oil-resistant insertion sheets, and gaskets. Coloured coated oil-resistant items can be produced using this elastomer. The low toxicity of this polymer also enables the manufacture of hygienic and food-grade conveyor belts, hoses and oil-resistant aprons.

### **2.1.5.1 Derivatives of Nitrile Rubber**

#### **(a) XNBR and Hydrogenated NBR (HNBR)**

(i) **XNBR** is a carboxylic-modified nitrile rubber which shows similar oil resistance as that of traditional NBR. It contains one or more acrylic-type acids as part of the comonomer system in addition to butadiene and acrylonitrile. These monomers develop a chain that resembles that of a normal nitrile rubber. The carboxyl groups which are distributed along the chain are usually observed every 100–200 carbon atoms. This modification gives the polymer vastly improved physical characteristics such as increased hardness, higher tensile and tear strength, improved abrasion resistance, better low-temperature properties, and better ozone resistance when compared with standard nitrile rubber (**Figure 2.1**).

XNBR also exhibits improved retention of physical properties after ageing in air and hot oil. XNBR can be vulcanised by using sulfur and accelerators in the presence of certain metal oxides because the polymer chains contain double bonds similar to that of NBR.

(ii) **HNBR** exhibits higher resistance to oxidation. It can tolerate a high service temperature of 150 °C.

HNBR is produced by removal of the double bonds in the main chain of the copolymer by hydrogenation. This polymer can usually be cured only by using peroxides because it contains the lowest level of residual double bonds needed for crosslinking. Some HNBR grades with double bonds  $\geq 3.5\%$  can be cured with sulfur [9].

These polymers are not generally used in textile coating applications. However, they are used in other engineering applications (except in some of the special fields of uses in which the service conditions are demanding and unchangeable for the coated textiles). Coating with these polymer mixes may follow the spreading system to obtain a good finish of the coated articles.

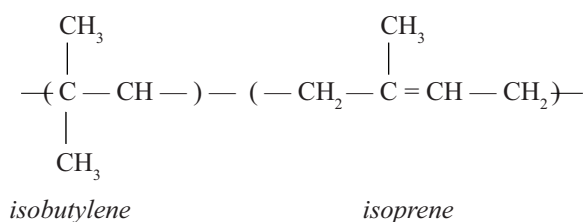
### **2.1.6 Isobutylene-isoprene Rubber (IIR)**

Commercially, isobutylene-isoprene rubber (IIR) is called butyl rubber. It is produced by the copolymerisation of isobutylene and isoprene with methyl chloride as the solvent and aluminium chloride ( $\text{AlCl}_3$ ) as the catalyst. The polymerisation is conducted at  $-100\text{ }^\circ\text{C}$ . A small amount of water (or  $\text{HCl}$ ) is added to act as a co-catalyst.

Anhydrous aluminium chloride is dissolved in methyl chloride and fed to the polymerisation reactor together with the mixture of isobutylene and isoprene.

The polymer is formed instantaneously as small particles of slurry. It overflows into a hot water tank and, with the help of a recovery system, methyl chloride and unreacted monomers are flashed off and recycled. A small amount of zinc stearate and antioxidant are added at this point to prevent (i) coagulation of the rubber particles and (ii) deterioration during finishing and storing. Wet polymer particles are separated from the slurry by vibrating screens, dried through a tunnel dryer, extruded and hot-milled. Finally bales are prepared in the machine for shipment.

To obtain a high molecular weight polymer, the polymerisation temperature must be kept low. It is very important to maintain low temperatures during polymerisation because the reaction is exothermic and instantaneous [11]. The structure of isobutylene – isoprene rubber is shown in **Figure 2.8**.



**Figure 2.8** Structure of isobutylene – isoprene rubber

The term used in commercially available butyl rubber, ‘mole percent (mol%) unsaturation’ (i.e., the number of moles of isoprene present in 100 molecules of the polymer chain) indicates the number of sites available for crosslinking. In general, 98 moles of isobutylene and 2 moles of isoprene are present in the molecule. This means that the number of double bonds necessary for vulcanisation using sulfur is present.

A wide variety of industrially used grades of IIR rubbers are available in a large range of different Mooney viscosities and at various levels of unsaturation. These are the grades of butyl rubbers which consist of 97-99.5 mol% of isobutylene with 0.5-3 mol% of isoprene. Grades with the highest mole percentage unsaturation have the fastest cure rates, but they also exhibit lower resistance to weather and ozone than more saturated grades.

Selection of the correct type of butyl rubber is dependent upon the desired physical properties, rate of curing, and processing behaviour. Low Mooney viscosities with low filler percentages and an appropriate amount of plasticiser can give smooth-finish calendered sheets using textile substrates. High Mooney viscosities offer a higher 'green strength'.

Coumarone-indene resins (10 phr) can be added to a butyl rubber compound to increase the green strength, which also improves the calendered surface finish of the coated sheet and increases the hardness of the stock. Addition of 3-5 phr of polyethylene into the compound helps to smooth the calendering surface and can reduce shrinkage.

IRR's unique properties make it suitable for applications in the technical and military sectors, which have demanding product requirements.

Some of the special properties that contribute to the unique elastomeric qualities of butyl rubbers in coated textile applications are due to their low level of unsaturation between the long segments of polyisobutylene:

- Very low permeability to air/gas.
- High abrasion resistance.
- High shock-absorption.
- Excellent resistance to weathering and ozone.
- High moisture resistances.
- High resistance to chemicals.
- Excellent electrical resistance.

IIR-coated textiles can retain gases. This impermeability is imparted by the polyisobutylene portion of the molecule of butyl rubber and its compact structure. When compared with the air-retention capacity of this polymer, it is about eight-fold better than that of NR.

They are also impermeable to carbon dioxide, hydrogen, nitrogen and helium. This special property, along with a very low brittleness ( $-75^{\circ}\text{C}$ ), make their coated fabrics very useful in some of the special application areas in the defence sectors.

The low level of chemical unsaturation in the polymer chain offers high resistance to ozone. Resistance to mineral acids is due to a low degree of olefinic unsaturation

in the saturated hydrocarbon backbone of this polymer. The saturated hydrocarbon nature of this elastomer also provides high resistance against moisture.

The primary importance of selection of IIR for coating applications is the correct grade of rubber from various grades of this polymer available commercially which can offer better processing properties, an appropriate rate of cure, and desired physical characteristics.

The gum tensile strength of butyl rubbers is high. Improved results of the mixes for textile coating can be achieved by the selection of fillers, processing aids and system of cure. Improved calendering behaviour can be obtained in selecting a low Mooney viscosity, low filler percentage, and incorporation of suitable plasticisers in the formulations.

To obtain high green-strength stocks, high Mooney rubbers with a high filler percentage are suitable. To obtain good physical properties and improved calendering during coating, FEF grade carbon blacks may be added as reinforcing filler. Incorporation of reinforcing mineral fillers in the IIR compound (e.g., silica, clays, talcs) may offer flexible coatings. Compounding with carbon blacks and mineral fillers can give very good calendering behaviour while coating. Coloured coatings can be designed using white fillers with the addition of rubber colours.

Addition of a coumarone-indene resin as a processing aid improves the surface finish. To obtain better calendering, incorporation of 5 phr of hydrocarbon oils of the paraffin type give good results. As a plasticiser to the mixes, the use of naphthenic hydrocarbon oils offers good calendering. To obtain good processing characteristics and better dispersion of fillers in the stocks, stearic acid, zinc soaps, fatty alcohol esters, and factices are added to IIR-based compounds. This elastomer is non-polar, so can accept high oils and paraffins, which results in a good surface finish of the coated articles.

Butyl rubber compounds can be processed in all types of conventional rubber-processing equipment.

For friction-coating mixes, the oil level may be increased to 10–15 phr to obtain softer compounds suitable for this purpose. In wet spread-coating applications, a solution can be prepared by dissolving the mix in solvents (e.g., hydrocarbon solvents) and the dough applied on fabric in a rubber-spreading machine if a base coating or very thin coating on the fabric is desired. Higher-gauge coating is also possible using the spreading process by increasing the number of coatings after adequate drying on completion of each coat.

The inherent property of resistance to ozone and weathering of this polymer may be increased further by incorporating antioxidants/antiozonants in the mixes. This will improve protection against heat and ozone (if necessary) for service conditions.

Butyl rubber-coated articles can be cured using rubber accelerators such as MBTS, MBT and ZDC. The proportion varies from 0.5 phr to 1.5 phr depending on the rate of cure in the presence of sulfur. To activate organic accelerators, zinc oxide is usually required. It can also be cured with phenol formaldehyde resins (which exhibit excellent heat-resistance and ageing properties) but this system is not normally used to vulcanise coated items.

This resin cure system requires a halogen-containing material such as stannous chloride ( $\text{SnCl}_2$ ) or a halogen-containing elastomer such as CR in butyl rubber compounds because of its low unsaturation.

The temperature for vulcanisation of textile-coated articles using this elastomer is 149-170 °C. To cure items of higher thicknesses, the temperature may be increased to 180 °C.

#### **2.1.6.1 Derivatives of Butyl Rubber**

##### **(a) Chlorobutyl Rubbers (CIIR) and Bromobutyl Rubbers (BIIR)**

Butyl rubbers are incompatible with diene rubbers. To overcome this disadvantage, a hydrogen per isoprene unit is replaced by a halogen. These elastomers are commercially available as chlorobutyl (CIIR) and bromobutyl (BIIR) rubbers. CIIR and BIIR have distinct advantages with respect to cure reactivity, state of cure, resistance to reversion (reversal of cure), and co-vulcanisation with diene rubbers.

CIIR is produced by introducing a continuous stream of chlorine gas in a hexane solution of butyl. BIIR is prepared by reacting bromine with butyl rubber.

The processing characteristics of CIIR are similar to those of IIR because of the more reactive nature of the polymer, but specific care must be taken while processing. Adjustment in processing conditions is necessary to release entrapped air (a common problem which occurs during calendaring because this is an impermeable polymer). The excellent properties of blending with other unsaturated elastomers, and its co-vulcanisation is possible with these rubbers. CIIR therefore offer versatility of use in coating for many applications. Similar to butyl rubber, CIIR also offer very low permeability to air and gases, heat resistance, and resistance to environmental degradation. In coating applications, the tack of the stock can be improved by inclusion of certain proportions of NR in the compound.



The characteristic features of bromobutyl and chlorobutyl polymers are essentially the same. Bromobutyl can provide a faster rate of cure because of its more active cure sites, and can offer better adhesion to unsaturated rubbers such as NR, SBR, CR, and NBR. To extend the range of properties, this rubber can be blended with unsaturated elastomers for utilisation in textile-coated products [10].

NR at 20–30 phr can be blended with CIIR stocks for use in dry calendering or in wet spread-coating of textiles to impart building tack. This blending provides adequate tack for the fabrication of articles from the coated fabric. Blending with SBR and PBR improves the flex life of the coated matrix. Addition of a phenolic resin in the formulation further improves the tack of the stock. This is necessary for the friction-coating of textiles to make use of technical and engineering products using the coated fabric.

### **2.1.7 Ethylene Propylene Rubber**

Ethylene propylene rubber (EPM) can be produced by copolymerising ethylene and propylene with certain types of Ziegler–Natta catalysts, and the resulting products are amorphous and rubbery (Figure 2.9). They do not contain unsaturation in the polymer chain, so they can be crosslinked only with peroxides. This copolymer is non-crystalline and has outstanding resistance to degradation. Commercially available EPM contain 40–80% of ethylene. The brittle point of this copolymer is  $-95^{\circ}\text{C}$  and the  $T_g$  is  $-60^{\circ}\text{C}$ .

EPDM is a terpolymer (Figure 2.10). It is polymerised from ethylene, propylene and a small percentage of diene. The latter provides unsaturation in the side chain or pendant to offer sites for crosslinking. The diene is provided not in the polymer backbone but in a pendant side group.

The manufacture of EPDM rubbers is conducted by two polymerisation processes: solution and suspension.

The most widely used system to manufacture EPDM is solution polymerisation. It is essential that all of the input materials used for polymerisation are dry. Solvent carrier hexane/pentane, monomers, and catalysts must be thoroughly dried because the catalysts used are very sensitive to water and polar materials.

No solvent is used in the suspension system of polymerisation, only an excess quantity of propylene serves as the solvent.

The polymerisation is conducted in two or three vessels. A continuous and measured

quantity of hexane, ethylene, propylene, diene, catalyst solution, and co-catalyst solution is fed into the first of a series of polymerisation vessels.

The polymerisation reaction is highly exothermic. Suitable arrangements are provided in the polymerisation vessels to control the temperature (chilled jackets and internal coils). It is necessary to control the temperature within narrow limits to obtain the desired average molecular weight and distribution of the final elastomer. To terminate the polymerisation reaction, a small quantity of water or alcohol is added.

To separate the dissolved rubber from the solvent, stirred boiling water is used to distil the solvent and the rubber in 'crumbs', which are then collected from the water. EPDM bales are made by compressing the dry crumbs.

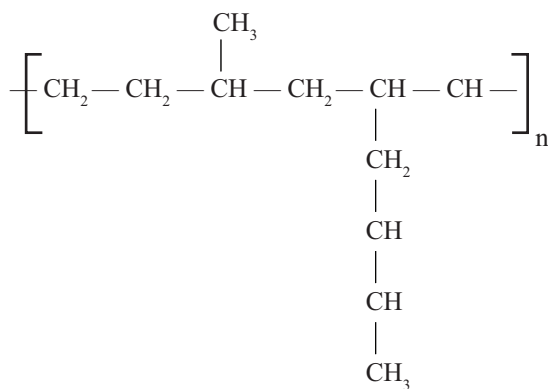
The resulting rubber has unsaturation and can be vulcanised with a conventional system of sulfur if a third monomer (diene) is added during the copolymerisation of ethylene and propylene.

Commercially available EPDM usually contain 4–5% by weight of diene and 30–70% of ethylene. The available Mooney viscosity of EPM is 25–35, and for EPDM it is 45–120 Mooney units.

There are three types of non-conjugated dienes used depending on the rate of cure in the manufacture of industrial-grade EPDM so that the double bond resides in the side groups of polymer chains.

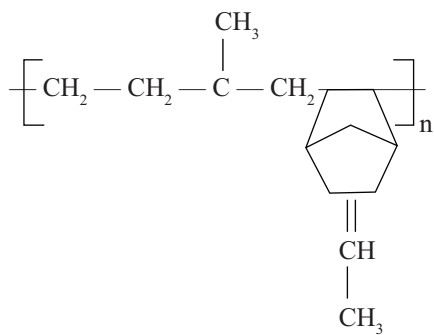
- (i) Use of dicyclopentadiene (DCPD) as a termonomer: 3-6 double bonds can be introduced per 1000 carbon atoms of the polymer chain. It exhibits a slow rate of cure.
- (ii) By introducing ethylidene norbornene (ENB) the rubber shows the fastest curing rate. It is possible to introduce 4–15 double bonds for each 1000 carbon-atom chain length and the polymer remains free of gel.
- (iii) In between DCPD and ENB, the third type of termonomer, hexadiene gives about 4-8 double bonds available for every 1000 carbon atoms. The resulting terpolymers can offer an intermediate cure rate [12].

A high proportion of ethylene or propylene in the rubber offers the higher tensile strength and elongation. On increasing the ethylene content, the final product shows increased hardness, high green strength, higher tensile strength, enhanced rebound resilience, and high thermoplastic properties. EPM and EPDM as well as terpolymers offer outstanding resistance to oxygen, ozone and UV exposure because of their saturated main chain.



Ethylene propylene 1, 4 hexadiene

**Figure 2.9** Structure of ethylene propylene 1,4-hexadiene



EPDM with ENB

**Figure 2.10** Structural formula of EPDM polymer

Some of the special properties of EPDM are:

- Very low specific gravity.
- Impermeability to gases and water.

- Excellent heat and ageing resistance.
- Resistance to UV and oxidative cracking due to ozone.
- Excellent low-temperature flexibility (very low brittle point and  $T_g$ ).
- Excellent electrical properties (resistance >25 kV).
- Very good mechanical properties, very high extendibility.
- Excellent resistance to chemicals.
- Good resistance to animal oil and vegetable oil.
- Very low moisture absorption and salt-water resistance.

Use of reinforcing carbon blacks or white fillers is essential to obtain good physical properties for EPM/EPDM. Both elastomers are compatible with petroleum oils of paraffinic and naphthenic types. Medium-viscosity oils can be incorporated in the stocks without greatly affecting physical properties. A higher proportion of ultra-fast accelerators and sulfur can cure EPDM-based compounds. Antioxidants and antiozonants are usually not necessary unless for highly demanding applications are required. Graphical representation of the reinforced tensile strength of EPDM rubber is illustrated in **Figure 2.1**.

Conventional rubber-industry equipment is used to process EPDM stocks. High-viscosity rubbers are tough and nery and provide resistance to molecular breakdown in mill mixing. However, they accept the high loading of fillers and oils, thereby improving the processing behaviour. The type of elastomer with a low Mooney viscosity shows improved processing characteristics during mixing in incorporating a high proportion of filler.

EPDM rubber compounds lack tackiness. This may create problems in adhesion during the coating application on fabric substrates and in building-up operations. Addition of a few parts of tackifier resins such as coumarone-indene resins, petroleum resins and plasticisers in the compound help in overcoming this deficiency.

EPDM can be suitably blended with other polymers. To impart ozone-resistance properties, high ethylene-containing EPDM can be blended with NR, SBR, and NBR. This blending system can be exploited in coated fabric applications to enhance resistance to the weather and ozone (particularly if the product is for outdoor uses). It can also be blended with polychloroprene and acrylonitrile butadiene rubbers to reduce the cost of the stocks, but with due consideration towards the resistance to hydrocarbon oils and solvents in the base polymers.

For textile coating applications NR at 20% can be incorporated with EPDM to increase adhesion with substrates.

Special curing agents such as dicumyl peroxide are required to obtain the appropriately cured saturated polymer EPM. Common rubber accelerators are suitable to cure the unsaturated terpolymer EPDM, but at a higher amount than that generally used for unsaturated rubbers.

Appropriately designed and carefully prepared compounds will not pose problems in coating fabrics by calendering. To obtain good calendering processability, the temperature of the feed stocks should be maintained in the range 80–100 °C and the speed should be ~30–35 m/min [10]. The properties of this elastomer are depicted in Table 2.4.

EPDM compounds can also be coated on natural and man-made textiles using a rubber-spreading machine. A dough of correct viscosity is prepared in aromatic hydrocarbon solvents. A conventional rubber-spreading machine is used to spread the rubber solution over the fabric by a knife on the roller system. This system is utilised if a very thin coating is necessary or as an anchor coat for subsequent coating on a calender. Multiple coats can also be applied to obtain better adhesion of the rubber layer with a cloth substrate, and to increase the thickness of the coating after the drying process of each coating. Drying is done by passing the coated fabric over steam-heated chests after each coat.

EPDM-coated fabrics are used to make many industrial products. Important areas are heat-resistant conveyor belts, hoses, gaskets, and in producing automobile components. EPDM-coated textiles are exclusively used in waterproofing and outdoor applications such as truck tarpaulins, inflatable items, pollution-control components, and liners for water-reservoir storage. Glass fabric coated with this rubber, fabricated in tubular form, is used for conveying hot flue gases and in various pollution-control equipments to exhaust gases.

### **2.1.8 Silicone Rubber**

A series of complex chemical reactions from the starting basic material (sand) and alkyl or aryl halide is necessary to produce silicone gums or polymer. On heating with carbon in an electric furnace, the sand or quartz ( $\text{SiO}_2$ ) is reduced to elemental silicone (Si). Then, in the presence of a copper catalyst, the silicone is converted to methylchlorosilanes by a direct reaction process with methyl chloride.

This reaction may be directed to produce dimethyldichlorosilane, which is the

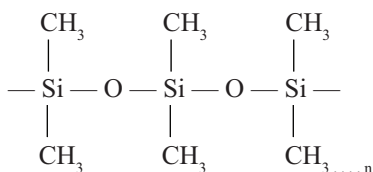
basic intermediate for producing dimethyl silicone gum. The difunctional dimethyl chlorosilane reacts with water to form siloxane polymers.

After addition of end-blocking trimethyl units, the polymerisation is terminated. Intermediates (e.g., phenyl/vinyl) in small quantities can be introduced in the copolymerisation process with dimethyl to make the resulting polymer more efficient to vulcanise by using peroxide as a crosslinking agent.

The methyl groups along the chain can be substituted by phenyl, vinyl or trifluoropropyl. A small number of vinyl or other functional groups are built into the macromolecules as ter- components. To an 'inorganic' backbone, the presence of 'organic' groups provides silicones a unique combination of characteristics, and enables use in different fields with useful properties. In obtaining a combination of properties, along the siloxane chain both phenyl and vinyl groups may be substituted for methyl groups [13, 14].

The resulting lower molecular weight polymers are in a liquid state and the higher molecular weight polymers are gums. Liquid silicones are the products of different commercial importance, particularly for the rubber-processing industry, and are widely used as releasing agents for rubber moulds. The structure of dimethyl polysiloxane is shown in **Figure 2.11**.

By crosslinking, it is possible to convert the gums into viscoelastic elastomers in the presence of organic peroxides.



**Figure 2.11** Dimethyl polysiloxane

The unique combination of properties of silicone rubbers are successfully exploited in various applications when used in coating textiles:

- Resistance to a wide range of temperatures.
- Resistance to chemicals.

- High abrasion resistance.
- Good mechanical properties.
- Excellent electrical properties.
- Resistance to UV, ozone, and the weather.
- Permeability to gases.
- Resistance to fungi and bacteria.
- Resistance to water.
- Inertness.

The most outstanding property of silicone elastomers is the ability to withstand a very wide range of service temperatures. Silicone elastomers can perform for extended periods from  $-100\text{ }^{\circ}\text{C}$  to  $300\text{ }^{\circ}\text{C}$  if appropriately compounded. The service life of this rubber is estimated to be  $150\text{ }^{\circ}\text{C}$  for 5-10 years, and to be  $120\text{ }^{\circ}\text{C}$  for 10-20 years; their properties remain stable during these times. No commercially available rubbers can approach this level of service life at this temperature [8] (**Table 2.4**).

At the low temperature limit, the  $T_g$  of silicone rubbers is  $-123\text{ }^{\circ}\text{C}$ . Silicone rubber elastomers have good resistance to oil and fuel as well as excellent resistance to chemicals. These rubbers have zero or very little effect on exposure to sunlight, ozone or oxygen. They have resistance to acids (e.g., acetic, hydrochloric, nitric and sulfuric) and bases (e.g., ammonium hydroxide, sodium hydroxide and concentrated sodium hydroxide).

Silicone rubbers exhibit high flexibility and insulation resistance at high and low temperature ranges in comparison with other flexible materials. The volume resistivity of silicone rubber is  $2\text{--}10 \times 10^{14}\text{ }\Omega\text{ cm}$ .

The unique properties of inertness of cured silicone rubber-coated textiles are odourless, tasteless, non-toxic, and non-staining to other materials. These characteristic features allow this rubber to be used in physiologically acceptable items. They are resistant to bacteria, fungi and soil chemicals, which is advantageous compared with other elastomers.

Gum silicone elastomers can be compounded with fillers, processing aids and curing agents suitable for the application of coating textiles. To achieve desirable processing and physical properties, high molecular weight silicone gums can be reinforced with fumed silica. This fumed filler gives excellent electrical properties, and contributes to the development of tensile and tear strength of the stocks with low water-absorbing

properties. The colouring agents incorporated in silicone rubber mixes for colour-coating applications have to be chosen carefully because organic pigments are not suitable for high-temperature uses. In such applications, inorganic pigments such as red iron oxides and for white articles, titanium dioxide may be used as colouring agents.

Carbon blacks are not generally recommended in silicone rubber stocks as reinforcing fillers because they may affect the activity of peroxides added as curing agents. Benzoyl peroxide (Crosslinking Agent CL 40, Bayer) is usually employed as the curing agent because of its high decomposition temperature and low vapour pressure. This permits the heat to remove the solvents in spreading-coated products. The plasticisers used as processing aids for silicone rubber mixes are silicone fluids of high molecular weight. Contamination with other chemicals of silicone rubber stocks may affect the curing characteristics. Hence, it is important to maintain cleanliness during the compounding and processing of silicone rubber.

The compounds based on silicone elastomers can be processed in standard rubber-processing equipment. It is possible to apply a thin coating of ~0.2 mm on textile substrates one side at a time by using three rolls on a line rubber calender machine. It is important to maintain the temperature of the rolls while coating with silicone rubber stocks:

- Top roll is at 50° C
- Middle roll is at room temperature
- Bottom roll is water-cooled

The conventional rubber calendering process can be implemented to coat silicone rubber stocks to one or both sides of the reinforcing fabric. It is necessary to adjust the speed of the calender machine depending on the surface nature of the coated materials. The speed of the machine should be maintained in the range 1.5-3 m/min.

Liners are used to get a smooth and non-sticking surface of the coated items. Liners of high melting point (such as polyethylene sheeting, coated paper, Holland cloth) and uncoated thin fabric liners if a mild fabric impression is acceptable, may be used. The recommended roll diameter of the coated fabric when vulcanised in roll form in a vulcaniser should be  $\leq 30$  cm.

Addition of 1 phr of polytetrafluoroethylene powder into the silicone rubber mixes will substantially improve the calendering characteristics of the compound.

In the process of friction coating of silicone rubber stocks on natural or man-made textiles using a three-roll calender, the lower two rolls run at uneven speeds. To coat



both sides of the substrate with silicone compound at a time, the four-roll rubber calender machine in an inverted 'L' or 'Z' configuration is suitable.

The spread coating method is applicable if a very thin coating on lighter fabric is desirable or to apply a foundation/anchor coating on pretreated man-made textiles with a bonding agent to obtain better adhesion with the subsequent coat in a calender.

The preparation of silicone rubber compound dough for use in spreading machine/dispersion coating involves the use of the following solvents: xylene, toluene, chlorinated hydrocarbons, or mineral spirits. A finished coating thickness in the range 0.2–0.35 mm is obtainable by the spread coating process; a higher thickness is achievable by increasing the number of coats. Proper drying is necessary after each single coating by passing over a steam chest fitted alongside the spreading machine. For the coating of fabrics by the dispersion coating system, the solution in the solvent with a lower viscosity is prepared for use in the dipping process. To obtain a higher coating thickness, the use of thicker dispersions is required. To maintain the thickness, using wiper blades, an adjustable gap is needed.

Natural/man-made woven fabrics coated with silicone rubber are utilised for different mechanical and electrical purposes. Reinforcement offered by the woven fabric and the elastomer coating provides resiliency, flexibility, electrical resistance and heat resistance along with resistance to moisture, weather and ozone.

Industrially used glass-woven cloth coated with silicone rubber offers high breaking strength when compared with the strength:weight ratio, good dimensional stability, virtually zero moisture absorption, and very good heat resistance. This product also provides high adhesion strength when the glass fabric is pretreated with a suitable bonding agent before coating. It also exhibits maximum electrical properties, which can be used in high-flex conditions.

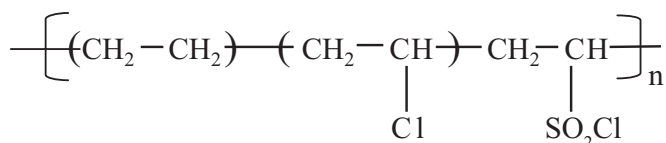
In the fabrication of high heat-resistant conveyor belts, silicone rubber-coated textiles are used in the unvulcanised state and subsequently the built-in belt is cured in rubber curing presses. Inflatable items, weather-protective covers, and industrial items can be made out of silicone elastomer-coated fabrics. Silicone rubber-coated glass textiles are utilised to prepare exhaust tubes for high-temperature air/gases in pollution-control equipment [14].

### **2.1.9 Chlorosulfonated Polyethylene Rubber**

Chlorosulfonated polyethylene (CSM) rubbers are produced by reacting polyethylene in a solution of chlorine and sulfur dioxide at 70–75 °C. The crystalline polyethylene

is converted into an amorphous elastomer with the use of varying amounts of chlorine. Along with the saturated polymer chain, sulfur and chlorine are randomly distributed and the resulting polymer can be processed and vulcanised like rubbers. Because of their fully saturated polymer backbone, these rubbers are highly resistant to weathering, ozone and degradation by chemicals.

The trade name Hypalon was introduced by DuPont (manufacturer of different types of CSM rubbers). This term is commonly used in the industry. Commercially, CSM polymers are available with varying amounts of chlorine (25-43% by weight). They offer a wide spectrum of physical and chemical properties in the range of Mooney viscosities and hardness. The chemical formula of CSM rubber is shown in **Figure 2.12**.



**Figure 2.12** Chemical formula of chlorosulfonated polyethylene

The outstanding characteristics of Hypalon rubbers have proved their suitability in some of the special applications in the coated-fabric industry because they maintain:

- High resistance against water, heat and the weather.
- Outstanding resistance to ozone.
- Excellent flame resistance.
- Very good flex and abrasion resistances.
- Excellent colour stability upon exposure to light.
- Good oil resistance.
- High resistance to corrosive chemicals.

These rubbers cannot be broken down in a rubber mixing mill but soften like thermoplastics in a warm mill. During calendering, the bowl temperature is to be maintained at 60-90 °C. Because of the thermoplastic nature of this polymer,

calendering can provide better release at higher temperatures. In building-up operations, using rubberised fabrics in unvulcanised states with a warm-up at 50-60 °C gives satisfactory results [14].

The fillers and plasticisers used in other elastomers can be used in CSM to obtain the desired physical properties of cured products. The polymer is chemically saturated and contains no double bonds, so antioxidants are not necessary for protection from oxidation. This inherent property enables this rubber to produce excellent colour-stable and weather-resistant products. The mechanical and other properties of this polymer are detailed in **Figure 2.1** and **Table 2.4**.

Incorporation of litharge in the compound provides resistance to water, chemicals and also exhibits a good compression set. Using zinc oxide in the compounding of CSM to eliminate the degradation reaction catalysed by the formation of zinc chloride is to be avoided. For bright colour applications, epoxy resins and magnesia may be added as compounding ingredients (which may also increase the water resistance of the product).

Bright colour rubber paints can be prepared using Hypalon 20/30 by dissolving coloured mill-mixed stocks made from these grades of polymer in solvents such as toluene or ketones. This type of paint can be cured if exposed to air and can be used to paint the exterior of rubber boats and other inflatable items made from rubber-coated fabric. This leaves a lightweight, elastic, crack-resistant, and weather-resistant membrane of paint on the surface of the coated products.

The coated fabrics made from CSM are weather-, water-, oil-, flame- and electrical-resistant. They are used in making tarpaulins, rubber boats, boat covers, radomes, inflatable structures, insulating blankets, and many other products used in industrial and military applications.

Due to its high electrical resistivity ( $10^{14} \Omega \text{ cm}$ ), excellent resistance to oxidative ageing, and because it does not support combustion, insulating blankets are made from coated textiles using this rubber for outdoor applications.

It is possible to apply very low thickness, brightly coloured coating on lightweight fabric using this elastomer in a rubber-spreading machine. A solution is prepared from suitably compounded Hypalon 30 (this grade is specially prepared to have low-to-medium hydrogen bond strength) by dissolving the compound in solvents.

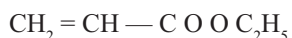
The prepared rubber dough can be applied to fabric using spreading machine for coating. To obtain a higher thickness of coating, the number of passes is increased after drying on a steam chest after each coating.

CSM has outstanding resistance to strong oxidising chemicals and acids. The textile coating (which is in an uncured state) is utilised to construct hoses to carry chromic, sulfuric and nitric acids. Owing to its heat resistance and colourability, coated textiles can be used in the production of hot conveyor belts carrying food products which are usually white in colour [15].

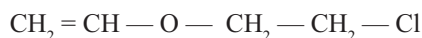
### **2.1.10 Polyacrylic Rubbers**

Polyacrylic rubbers (ACM) are copolymers of ethyl acrylate. They have ~95–99% of the polymer and a small percentage (5%) of cure sites which are halogen with chlorine (e.g., 2-chlorethylvinylether). They have a saturated backbone but can be cured with copolymerised reactive sites. Monomers that do not contain chlorine are also used by some manufacturers. The speciality elastomers ACM have high heat- and oil-resistant characteristics.

The methods used in producing ACM comprise (i) emulsion; (ii) suspension; (iii) solution; and (iv) bulk systems. The most common system type is the peroxide or persulfate thermal-initiated free radical type. Polymerisation consists of a batch system or a continuous process. To produce high molecular weight polymers, polymerisation is followed by emulsion and suspension. The solid polymer is obtained after coagulation from latex, washed, and then dried using hot air, vacuum or by extrusion techniques. Commercial polyacrylics are available in the form of white slabs, powder or crumbs in the Mooney viscosity range of 25-60 and specific gravity 1.1. The solution grades of these elastomers are also available. The polymer is soft, tacky and nervy. It has very good stability if stored in dry conditions even at 148 °C. The formula of polyacrylic rubber is shown in **Figure 2.13**.



ethyl acrylate



chlorethylvinylether

**Figure 2.13** Formula of polyacrylic rubber

Appropriately compounded polyacrylics can exhibit the following outstanding properties:

- Resistance to wide range of temperature –40 °C to 200 °C.

- Excellent flex life.
- Very good resistance to swelling in oils and aliphatic solvents at elevated temperatures.
- Inherent resistance to oxidation and ozone (even at higher temperatures).
- Very good resistance to discolouration under sunlight and weathering.
- Resistant to permeability of many gases.
- Wide range of hardness (available from 40 to 90 Shore A).
- Tensile strength can be achieved up to 170 kg/cm<sup>2</sup>.
- Elongation at break at ~400%.

The ethyl acrylate type shows the best overall balance of processing characteristics, physical properties, and resistance to heat and oil.

The soft and thermoplastic properties of polyacrylic elastomers enable them to soften easily during mixing.

Appropriately compounded ACM, if included with reinforcing fillers and a high state of cure, can provide the desired hardness, tensile strength, modulus, high elongation and good flex-resistance properties (**Figure 2.1**). The most effective fillers are reinforcing carbon blacks such as high-abrasion furnace black and FEF blacks. For white/light coloured compounds, precipitated silicas and calcium silicates can be the correct choice. Excellent resistance to discolouration of this polymer is not affected by UV light, oxygen and ozone. This elastomer is not only highly resistant to abrasion, but this property can be improved by incorporation of high-abrasion furnace blacks.

ACM rubbers are resistant to high temperature in combination with good physical characteristics such as compression set and oil resistance. Hence, they can be suitably used in coating textiles in the making of oil hoses, transmission belts, fabric coating for automobile gaskets, lightweight waterproof rain jackets, snow jackets, and life vests.

To increase the tackiness of compounds, high-melting-point coumarone-indene resins or partially aromatic resins such as alkylphenol acetylene resin (Koresin, Akron Chemicals) can be added in the stocks because these rubbers have low inherent tack. Building tack for fabricated items can be improved by using plasticisers and resins together.

Some of the newer varieties of polyacrylic elastomers have improved water resistance in comparison with earlier grades. Care must be taken to avoid acidic materials in compounding ingredients because these polymers are greatly affected by alkali and acids. Stearic acid should be restricted to 1 phr, which will not affect the cure.

The soft and thermoplastic properties of polyacrylic elastomers mean that they soften easily during mixing. Incorporation of reinforcing fillers at the early stage of mixing is necessary to obtain adequate dispersion.

Breakdown of this type of rubber is not necessary for incorporation of the compounding ingredients. In open mill mixing, forming a band in a cool mill is necessary to facilitate the incorporation of ingredients. Mixing in a Banbury mill can also be employed, and the stock temperature must be maintained at 70-90 °C.

Suitably formulated ACM rubber compounds can be used as coating textiles in a conventional rubber calender machine. To obtain good calendering properties, an additional amount of lubricants may be necessary. Before feeding into the calender machine, a warm-up operation in two open roll mills is required to obtain the desired uniform flow properties while coating. To obtain improved coating characteristics, the temperature of calendering should be maintained at 37-70 °C [9].

A three-roll calender is used for coating textiles on one surface on a single run. To obtain the best calendering on textile coating, the temperature differential should be maintained as follows for one side at one operation:

- Top roll should be 60–70 °C
- Middle roll should be 70–80 °C
- Bottom roll should be 80–104 °C

Upon control of the temperature and gauge of the coating, a film thickness of this polymer as low as 0.25 mm can be obtained.

Some of the industrially available grades of polyacrylic elastomers, such as the ethyl acrylate types, can be dissolved in solvents such as methyl ethyl ketone and acetone without treatment in the mixing mill. The solubility parameters can also be enhanced by milling in a rubber mixing mill, and a suitable solution prepared for coating textiles. It is a major application for polyacrylic rubber in the form of solvent solutions. The prepared solution can be used for coating on textile fabrics utilising a conventional rubber spreading machine.

Curing to the saturated backbone polyacrylic polymers is possible through the small percentage of copolymerised reactive cure sites. Several cure systems have been developed to cure specific types of commercially important polyacrylic rubbers [14].

A common system used for vulcanisation of reactive polyacrylics is the soap/sulfur system. Sodium or potassium stearate is used as a curative and the sulfur acts as an accelerator. Addition of stearic acid into the curing system will retard the cure because of its acidic nature. However, the cure can be accelerated by using magnesium oxide as a base. The most effective cure system of polyacrylic elastomers may be obtained by incorporation of metallic soaps, a sulfur donor and a hexamethylene diamine carbamate-type accelerator (Diak #1). Use of red lead and ethylene thiourea (NA22, DuPont) is also incorporated in industry.

Another system that is also effective involves using alkali metal stearate, sulfur or a sulfur donor and zinc dimethyldithiocarbamate with ammonium adipate. Using potassium stearates is more effective if the curing temperature is 175 °C. The effectiveness of vulcanisation can be improved by including sodium stearate and potassium stearate into the compound.

The vulcanisation temperature can be maintained at 145–170 °C, but the duration of cure may vary depending on the coating thickness of the product.

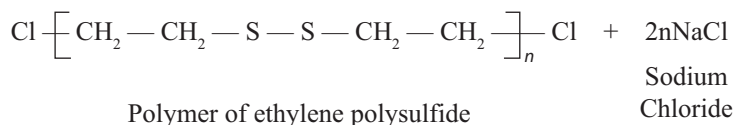
Textiles coated with polyacrylic rubber compounds are used to make hoses, belts and packaging, as well as rainwear, snow jackets and other protective garments.

### **2.1.11 Polysulfide Rubber**

The process of manufacturing solid linear polysulfide rubber (Thiokol, ATK Launch Systems Group) is by heating and stirring aqueous sodium polysulfide solution with the addition of an organic dihalide. The polycondensation temperature is maintained at 60 °C and the polymer is formed. Commercially used dihalides include dichloroethyl formal and ethylene dichloride. The readily available ethylene dichloride is produced from ethylene and chlorine. The ethylene chlorohydrin is formed by reacting ethylene oxide with hydrochloric acid. It is then reacted with formaldehyde to form the desired formal. The sodium polysulfide is produced by reacting sodium hydroxide with sulfur.

For the formation of the polymer in small granules, dispersing agents must be present in the solution. The polymeric product in a dispersed state is washed from the soluble salts. The dispersion is coagulated with acid to obtain high molecular weight elastomers. The terminal of the polymer chain can be created by hydrolysis

of the organic dihalide during polymerisation. The formic acid (FA) grade of millable gum polysulfide rubber is a copolymer of ethylene dichloride with dichloroethyl formal, and the resultant polymer contains 49% of sulfur. The structural formula of polysulfide polymer is shown in **Figure 2.14**.



**Figure 2.14** Structural formula of polysulfide rubber

This rubber is commercially available in two forms: (i) high molecular weight rubber and (ii) low molecular weight fluids or pastes.

Polysulfide rubbers can be processed in conventional rubber equipment. During mill mixing, this elastomer can be plasticised chemically using 0.1 phr of MBTS. It can also be processed in a Banbury mill, and the mill temperature should be maintained at ~65 °C. The compounding ingredients are added slowly to obtain a good dispersion in the mix. The vulcanisation system of this polymer is simple. It can essentially be cured by using zinc oxide in the mix. To increase the state of cure, the amount of zinc oxide can be increased to up to 10 phr. Inclusion of common rubber accelerators such as tetramethyl thiuram disulfide and DPG along with zinc oxide and a small dose of stearic acid into the compound provides a curing system of FA grade [5].

Polysulfide rubbers have poor inherent building tack. For improvement of the building tack of the compound, incorporation of 5 phr of cumarone resin helps to overcome this problem. Reinforcing carbon blacks such as SRF or FEF are used to increase the physical properties (**Figure 2.1**). In non-black compounds, fillers such as barytes, titanium dioxide, and lithopone are used. Stearic acid in the formulation will help to eliminate sticking of the compounds to mill rolls, and to facilitate processing. Facticees can be incorporated in the mix as process aids.

The excellent solvent resistance of polysulfide rubbers is an important characteristic. FA-grade polysulfide rubber has outstanding resistance to solvents such as ketones, esters and most aliphatic and aromatic solvents, as well as resistance to dilute acids and alkalis. To increase solvent resistance, blends with non-solvent-resistant elastomers



with this rubber can provide resistance to a certain group of solvents. IIR blends with this rubber may offer good resistance to solvents.

Coated fabrics comprising polysulfide elastomers can provide extremely low permeability to gases, organic liquids and water. They also offer excellent resistance to ozone, UV light, ageing and weathering. They can be serviceable in the temperature range  $-45^{\circ}\text{C}$  to  $93^{\circ}\text{C}$ .

The cement/putty based on FA polysulfide rubber compounds can be prepared by dispersing in ethylene dichloride solvent. These putties are used in leak-proofing applications on the joints of coated fabricated tanks and reservoirs used for storing oils and fuels. It can remain flexible in the temperature range  $-29^{\circ}\text{C}$  to  $120^{\circ}\text{C}$  without hardening or cracking upon long exposure [14].

The coating of textiles can be processed by preparing a solution of compounded FA polysulfide rubber in ethylene dichloride and applying it on fabrics in a rubber-spreading machine. Adjustment of the speed of the spreading machine roll as well as the solvent drying chest temperature is necessary to obtain a good coating surface. Coated fabrics with this elastomer are used in the inner liner of hoses used for conveying fuels. A very thin calender coating on fabrics is possible with polysulfide rubber subjected to suitably formulated stock with adjustment of the conventional calendering system and the temperature of the rolls.

A special application of this elastomer is a type of special paper coated with FA polysulfide rubber-based solution by a spreading or dipping process. The coated paper is used in the making of automotive gaskets which can withstand high resistance to oil and ageing [14] (Table 2.4).

### **2.1.12 Reclaim (or Regenerated) Rubber**

Reclaim or regenerated rubber is produced by the treatment of vulcanised scrap rubbers such as tyres, tubes and miscellaneous waste of rubber articles. They are ground to the desired mesh and cleaned. Metal and fabric particles are removed using chemical agents. The application of heat results in devulcanisation of the polymer. This process is essentially depolymerisation, and the combined sulfur is not removed. The resultant product can be processed, compounded with the virgin elastomer, and revulcanised in the usual manner.

The molecular weight is reduced and chain scission occurs during reclaiming of the vulcanised rubber scraps. When it is depolymerised, a break in the molecule of crosslinked rubber takes place.

Reclaim rubber is widely used as a raw material. It is available at a much cheaper cost than the original rubber. It can replace a substantial proportion of new rubber (natural and synthetic) without greatly affecting the physical properties of the compound. Nevertheless, tensile strength, tear resistance, resilience and abrasion resistances are reduced if an increased proportion of reclaim rubber is used in the mixes [14].

Commercially, different grades of reclaim rubbers are available. In coating applications, the fine grain extrusion quality reclaim rubber is the most suitable. This is added in a certain proportion to the compound based on the original rubber (natural and synthetic). It can be compounded with the virgin elastomer and used in textile coating applications, particularly if low cost, economical coated products are the requirement.

There are various methods of producing reclaim rubber commercially. However, the following are the important industrial methods:

- Digester process
- Pan process
- Reclaimator process

If heated for prolonged periods to 200–250 °C, vulcanised waste rubbers depolymerise and reclaim rubber is produced. This can be reused with the original rubber mixes. The process can be accelerated by the addition of chemicals or reclaiming agents:

- Thiophenols and disulfides.
- Dicyl disulfide or alkylated phenylsulfide (used for synthetic rubber vulcanised waste).

#### **(i) Digester Process**

Cured rubber scraps are cut to 6–8-mm pieces. They are freed from fabric and metal (removed by a magnetic separator) and loaded into a digester. Water, oils and other additives are added. The mixture is heated with steam to 198 °C, and maintained at this temperature for 4–12 hours with continuous agitation.

The digester is then ‘blown down’ and the contents deposited onto a conveyor. The stock is then conveyed to an extruder for straining and refining. It is then deposited onto a drum from which it is removed in slabs.

#### **(ii) Pan Process**

In the Pan Process, raw material produced from vulcanised waste ground into small

particles, and free from fabric fibres is then mixed with oil and other ingredients. The mixed material is then transferred to a steam heated vulcaniser where steam heating is carried out at 14 kg/cm<sup>2</sup> at 195 °C. The stock is unloaded after devulcanisation and conveyed to a mill for refining and straining using conventional methods. This method can be employed in reclaiming NR, SBR, CR, NBR and IIR.

### **(iii) Reclaimator Process**

The reclaimator process is employed to produce major quantities of reclaim rubber commercially. Fibre-free vulcanised rubber scraps are ground (30 mesh) and heated at 200–260 °C. The devulcanisation of rubbers occurs on rapid heating of the stocks. To achieve the desired plasticity, the time taken is 3–6 minutes. The rapid increase in plasticity is obtained by incorporating additives such as plasticisers and catalytic agents in the presence of oxygen [4, 14].

The reclaimator machine used for this process is a specially designed screw extruder with an adjustable clearance of the discharge head. At the hopper, the rubber crumbs are mixed with oil and chemical agents fed automatically for continuous reclaiming in the machine. It generates heat by mechanical methods for depolymerisation. To control the reaction, the discharge head clearance is adjusted.

The total cycle time is only 30 minutes. To maintain product quality, the time and temperature of processing are closely controlled. Depolymerised material is then mixed with processing and reinforcing agents, sheeted, and finished into slabs for industrial use.

Commercially available reclaim rubber is usually black. However, drab and white-coloured reclaims are also available for use in coloured mixes, which can be used for fabric coating. Drab/white reclaim rubber is produced from non-black scrap rubbers. Latex rubber made manufacturing wastes is usually the feed material for this type of reclaim. This includes hand gloves, condoms and other products made from latex.

The digester process is usually employed to make coloured reclaim. A small amount of caustic soda may be added if fabric is present in the scraps to digest it. Heat treatment is usually 8–12 hours under steam pressure of 14 kg/cm<sup>2</sup> at 195 °C. It is then processed for refining and sheeting, and slabs made in the usual manner.

Scraps from other specialty rubbers such as CR, NBR, and SR can also be reclaimed and may be used with the original rubber-based mixes for use in coating applications. The butyl rubber reclaim (made from butyl inner of tyres) has substantial commercial importance. This compound can give a smooth, good surface finish and faster calendaring when compared with the virgin butyl rubber mixes.

The following list details the processing advantages of using reclaim rubber in the coating compound:

- Shortens breakdown time and mixing time; dispersed well in virgin rubber due to low nerve.
- Lower power consumption during mixing.
- Low-temperature development during mixing and calendering.
- Faster and uniform calendering; controls dimensional stability.
- Increase and retain tack of the compound.
- Better penetration of the stock into the fabric; improves adhesion between fabric and coating.
- Low swelling and shrinkage of the compound while coating in the calender.
- High rate of cure.
- Lower compound cost.

The reclaim rubbers utilised in black or coloured compounding for textile coating purposes should have the standards for testing in the following parameters:

- Specific gravity.
- Polymer content.
- Proportion of carbon black.
- Plasticity.
- Characteristics of staining (in the case of coloured mixes).
- Calendering rate and properties.
- Odour/unpleasant smell.
- Rate of vulcanisation.

The usual shrinkage of high virgin rubber content stock is 6–10%; use of reclaim into the compound helps to reduce this problem. Because of less nerve, less internal heat builds up during mixing and calendering [5].

Fine grain (extrusion-quality) reclaim rubber may also be used if compounded with

the virgin rubber for spreading the coating of a fabric in a rubber-spreading machine by preparing a solution in suitable solvents [4].

Reuse of rubber waste contributes to substantial management of environmental pollution.

The coated fabrics utilised in products in which mixes contain reclaim are:

- Coating of textile/cords used in making cycle tyres, two-wheeler tyres and car tyres.
- Conveyor belts and tyre carcasses.
- Textile-reinforced hoses.
- Rubber insertion sheeting.
- Rubber textile composite used in flooring/mats/pathways.
- Ground sheets.
- Double-textured coated fabric sheeting.
- Bedspreads, hospital sheeting and aprons (usually white or coloured).

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# 3 Criteria for the Selection of Rubbers for Coating: Physical and Chemical Characteristics

**Bireswar Banerjee**

## 3.1 Introduction

A broad overview of the processing characteristics, chemical, oil and solvent resistance, as well as the electrical and mechanical properties of different elastomers used for the purpose of textile coating will be discussed in this chapter. Polymer technologists in the fabric-coating industry have to alter the parameters in elastomer processing to achieve the correct viscosity for the elastomer to function appropriately at the processing temperature. They also have to alter the rate of flow, applied stress and deformation, and rheological behaviour during calendering. Correcting the blend of polymers to obtain the desired characteristics of the composite is also important.

Dispersion of powdery chemicals and fillers in the elastomeric binder may require dispersing agents during the preparation of compounds to facilitate good processing. These may include resins, process oils, pine tars for high carbon black/white filled compounds, and particular plasticisers for synthetic elastomers. There are different kinds of process aids used in rubber compounding to improve processability. These include fatty acids, esters of fatty acids, fatty acid metal soaps, and low molecular weight resins [1].

At the initial stage of mixing of a compound, high shear stress and high energy is necessary. This can be significantly reduced by using chemical peptisers. It reduces the viscosity of the compound due to mechanical breakdown. This results in a reduction in energy consumption during mixing and improves the uniformity of the compound. Some synthetic elastomers can be treated with peptisers to reduce viscosity, but many synthetic elastomers can only be heat-treated during mixing before the incorporation of ingredients. Good processing and physical properties of mixes are achievable if all the compounding ingredients are dispersed well, and a homogeneous compound is prepared for subsequent flawless processing. For coloured rubber coatings, the powdery colour should also be well dispersed in the composition to obtain the desired prominence of colour shade. This is particularly important if a mixture of powdery pigments is used to obtain a specific shade of integrated colour [2].



Adhesion between the textile substrate and rubber matrix is the most essential requirement of elastomer-coated fabrics. Adhesion must be sufficiently strong and the composite should provide the desired mechanical properties. Surface characteristics and finishes are primarily dependent upon adhesion. A good finish and surface reactivity can be achieved in the way of (i) chemical bonding by a chemical reaction through the adhesive, fabric and rubber matrix; and (ii) molecular bonding of the composite: this event is highly dependent upon the property of the fibre [3].

### **3.1 Selection Criteria for Rubber Coating on Textiles**

The criteria for the selection of elastomers and additives processed for the coating of textiles are the significant factors for the choice of the correct type of rubber, and are the principal ingredients to meet the specific end-product requirements [4]. The essential elements to be taken into consideration are:

- Processing characteristics
- Curing characteristics
- Service condition
- Minimum and maximum temperatures of service
- Duration of service
- ‘Bondability’ with textiles
- Physical and chemical properties
- Resistance to water, acids and alkalis
- Resistance to the environment
- Resistance to oils and solvents
- Resistance to insecticides
- Economics of compounding
- Odourants and perfumes

#### **3.1.1 Processability**

Polymers comprise long chain molecules with repeating units, usually on a carbon

backbone. They are high molecular weight compounds, and highly viscous. Hence, it is necessary to reduce the molecular weight and viscosity to facilitate easy processing of the rubber compounds. Reduction in viscosity and increasing the plasticity of the elastomers generally used for coating applications can be obtained by mechanical milling. This can be achieved using open two-roll rubber mills or internal mixtures (Banbury mill). This primary process is required for incorporation of the fillers, liquid processing aids, and other compounding ingredients to prepare a homogeneous compound of desired plasticity which is to be further utilised in the coating of various types of textiles.

The term 'processability' refers to the exhibition of desirable properties after compounding to produce the final product. All the compounding ingredients should be uniformly dispersed in the rubber matrix, and should offer consistent rheological properties to achieve the ultimate quality of the product. A prepared mix of rubber is highly viscous and behaves as a non-Newtonian liquid.

The viscosity or plasticity of the rubber mixes contributes to its resistance to flow as well as safe processing time to initiate crosslinking of the elastomers under operational conditions.

Mastication of natural rubber (NR) is conducted in an open rubber two-roll mill or in an internal mixer. Due to repeated mechanical deformation in the presence of atmospheric oxygen, reduction of the molecular weight of the rubber takes place, and the rubber becomes increasingly plastic. Incorporation of compounding ingredients is possible at this stage upon further mixing. The diene rubbers of synthetic elastomer groups such as styrene-butadiene rubber (SBR), nitrile butadiene rubber (NBR), and polychloroprene (CR) can also be treated similarly to NR.

Addition of chemical peptising agents such as pentachlorothiophenol with dispersing additives (Renacit VII, Bayer) and zinc-2-benzamidothiophenate (Pepton 65, Anchor Chemical) in the mastication process of rubbers can accelerate the molecular breakdown of rubbers at lower temperatures. The normal amount of peptisers used is 0.2–0.5 phr; a higher proportion ( $\leq 2$  phr) may be necessary for synthetic rubbers.

The temperature of mill mastication may be maintained at 70 °C for NR, and a higher temperature (150 °C) may be necessary for synthetic elastomers. This may efficiently reduce the mastication time, thereby increasing the productivity, resulting in savings in energy and manpower.

The use of processing aids in the compounding (e.g., petroleum-based process oils, plasticisers, resins, factices and zinc salts of unsaturated fatty acids, internal lubricants, waxes, tackifying resins, and tars) significantly improves the processing properties of

natural and synthetic polymers used for the coating of textile fibres by dry calendering or by a wet system of spreading/dipping processes.

Waxes, octadecyl amines, and fatty acids can be used as processing aids in natural and synthetic rubbers such as SBR, polybutadiene (PBR), nitrile, CR and ethylene propylene diene (EPDM).

The use of zinc soaps of higher fatty acids (Struktol A60 or Aktiplast, Schill and Seilacher) help in the prevention of mill sticking during compounding, and on calender rolls during coating operations. These chemical agents can also help in the dispersion of fillers, and improve the flow behaviour of the mixes during processing [5].

Incorporation of 2–3 phr of fatty acid soaps/aliphatic fatty acids or blends of fatty acid derivatives may offer improved dispersion of fillers in synthetic elastomer-based compounds such as CR, NBR and EPDM. These chemicals also effectively improve flow properties and calendering operations as well as providing a better surface appearance and dimensional stability of the coating matrix.

To facilitate the processing of rubber compounds, resins such as coumarone–indene resins (CI resins) play an important part in aiding the incorporation of fillers during mixing, and improve the surface finishes on calendering at higher temperatures. Wood rosin can be used particularly in NR-based compounds to improve tack, but its use can be restricted because of its acidic nature [6].

The time allowed to pass through processing in mixing and calendering at high temperatures is directly dependent on the heat history of the processed compound.

The influence of heat starts from the mixing and storing conditions of the compounded sheets, then to treatment in the warm-up mill before calendering, and then to the elevation of temperature during preparation of the dough in the churner/mixer for use for spreading coating. These influences are cumulative. These may influence the reduction of processing safety, but this may not be evident in changing the plasticity of the stocks.

The important factors responsible for providing trouble-free processing of rubber compounds used in coating fabrics are:

- Appropriate viscosity to improve flow properties.
- Adequate green strength upon handling.
- Control shrinkage.
- Appropriate tack to provide adhesion with the substrate.

To obtain a uniform coating thickness during the coating operation in the calender machine, the viscosity of the stock must be constant. Rubber compounding is affected considerably by the temperature of the calender rolls and the compounds, and these need to be controlled precisely.

The prerequisite properties of good processability for coating applications may not be obtainable in the selection of a single elastomer-based stock, but the alternative is a blend of rubbers which can provide the appropriate processing characteristics.

It is essential to select the correct polymer (or blend of elastomers) which shows the desirable properties for compounding, in the warm-up mill, and in the calender machine when the dry process of coating is operated. In coating applications administered by a spreading machine, the solution/dough viscosity should be uniformly maintained throughout the process to prevent percolation of the solution from the fabric surface [7].

Unsaturated hydrocarbon-based polymers such as NR and SBR offer good processability. The high gum tensile strength of NR can be further enhanced by adding reinforcing fillers such as carbon blacks and silicas. Similar fillers can be added for low gum tensile SBR for increasing the strength.

For critical application areas of very high abrasion resistance, NR blended with PBR provides good results. Incorporation of the fast extrusion furnace black (FEF) offers improved calendering characteristics. Processing aids such as CI resins, petroleum resins, and phenolic resins, when added to NR-based compounds in small proportions, help in the dispersion of fillers, improve calendering, promote adhesion with textile substrates, and increase tear resistance. Petroleum oils which are low aniline point, aromatic types are generally used to improve the processing of NR-based compounds to obtain good dispersion of powdered fillers, and to maintain the viscosity of the mixes for further processing.

The oils added to rubber compounds as processing aids act as softeners to provide appropriate viscosity to the mixes to obtain the desired processing behaviour. Petroleum oils work as extenders to the elastomers, assist in the incorporation of fillers, and therefore make the product cheaper. They can be of paraffinic, naphthenic, or aromatic types. This classification is dependent upon the viscosity gravity constant of the oil [2].

In the manufacture of products using butyl rubber and EPDM elastomers, the paraffinic type of process oil is suitable. It is most suitable in the mixes for coating coloured articles because of its non-staining nature and lack of effect on the ageing process.

Very good processability is provided by aromatic process oils if used in NR and in some synthetic rubber compounds. Its low cost is also a considerable factor in compounding. With respect to processing properties, naphthenic process oils can be categorised in between the paraffinic type and aromatic type.

Increased level of tack for friction coating of NR may be achieved by: extra milling of the rubber; addition of resins, pine tar, or wood rosin as tackifiers; and addition of a liberal amount of petroleum process oil. If friction coating is necessary for subsequent coating in a calender, it is better to select NR in comparison with other general purpose synthetic rubbers. Adequate tack is also required in assembling a number of plies of coated textiles in the manufacture of conveyor belts, footwear and tyres obtainable if using this elastomer.

There is a tendency for premature curing or scorching of the compounds while processing for coating because of the high degree of unsaturation in the polymer chain of NR. This is also evident in some of the synthetic rubbers mixes if low structure reinforcing carbon blacks are added, and if they are formulated with faster curing accelerators. To overcome this problem, and to allow processing safety of the mixes at high temperature (i.e., extension of scorch time), the addition of rubber retarders such as cyclohexyl thiophthalimide, nitrosodiphenylamine (Vulkalant A, Bayer) and benzoic acid at 0.1–0.3 phr can provide an adequate safety level. Addition of factices in the formulations can give excellent processing, offer dimensional stability and shows a very good surface finish of the calendered coated products.

NR-based compounds can be dissolved in hydrocarbon solvents, and application of a very small amount can be spread on the fabric using a rubber-spreading machine. Solution coating by a dipping process is also possible. Both these processes can be applied as anchor coating on textiles, and to improve proofing for improved adhesion property with the subsequent coating in the spreading machine or calender. The spreading coating system will also provide good proofing against water, air, and gas of the finished coated textiles.

The inherent characteristic of CR is its crystallinity. To get trouble free coating selection of easy processing CR will produce good results. The polychloroprene rubbers tend to stick on the rolls during mixing. This problem can be prevented by using an extra amount of stearic acid or zinc soaps fatty acids in the formulation. Use of PBR (5 phr) in the mixes may also prevent sticking to the mill and calender roll, as suggested by the CR manufacturers.

CR, if formulated with the appropriate fillers and processing aids (e.g., factice) can provide a very good calendering finish and dimensional stability to the coating. When

compounded with a certain proportion of low viscosity elastomer with an increasing quantity of filler, factice and plasticisers, it further improves the dimensional stability of calender coated products.

Improvement in processing can also be obtained in CR by using aromatic mineral oil-based plasticisers in low-cost compounds. Synthetic plasticisers facilitate good processing, help in the incorporation of fillers, and improve the flexibility and resilience of the coated compound. Plasticisers are incorporated if petroleum oils are incompatible with the polymer.

Plasticisers of organic acid esters or phosphoric acids are particularly suitable for NBR and CR elastomers. Chlorinated paraffin hydrocarbons can be used as plasticisers in CR stocks. The use of this product can also enhance the non-flammability characteristics of the polymer [8].

In the process of spread coating, appropriately compounded CR can be dissolved in solvents such as toluene, methyl ethyl ketone or in ethyl acetate. The resulting dough can be spread on textiles using a rubber spreading machine.

The processability of NBR-based stocks for coating various types of plasticisers has considerable effects on: (i) adhesion with substrates, (ii) reduction of viscosity of the compound, (iii) improvement in calendering properties, and (iv) the flexibility of the final product. Improvement in tackiness of the compound can be obtained by using CI resins along with the plasticiser.

Nitrile rubbers have no inherent tack, so the use of resins and plasticisers together in the mixes substantially improves adhesion with the textile substrate, and also increases the building tack for the fabricated items in the uncured state. Besides increasing the tack, resins also help in the dispersion of fillers in the NBR mixes.

To achieve improved calendering, dimensional stability, uniformity of thickness of the coating, and overall finishes of the surface, oil-resistant factices may be added to the NBR-based compounds in the appropriate proportion. Ester/ether-type synthetic plasticisers can enhance the resilience of the compound. Use of resinous plasticisers in synthetic rubber mixes adequately increases the adhesion and building tack of the coated textiles. It also helps in dispersing light-reinforcing fillers such as fumed silica and low-structure blacks in the mixes for making coloured or black coatings.

Aromatic polyether plasticiser (Plastikator FH, Bayer) can also act as a good dispersing agent for light fillers, and can provide good tack to obtain better adhesion with the substrate. This plasticiser can also be used in nitrile rubber, CR, and butyl rubber compounding.

The incorporation of phenol formaldehyde resins in nitrile rubber formulations offers reinforcing and hardening, and can offer excellent flow during calendering. This resin can also be used as a tackifier for other synthetic rubber stocks utilised for coating.

For elastomers which have a very low tack such as polyacrylate rubbers, resins such as coumarone – indene resin, and Koresin (GAF) in the formulation, can act as good tackifying agents.

Difficulties may arise in processing NBR stocks in a calender coating system. An alternative method is to follow the wet coating process or spreading system. This is done by preparing a viscous solution of an appropriately designed mix in solvents (e.g., acetone, methyl ethyl ketone, toluene or xylene) and applying the dough on the textiles in a spreading machine. This system of coating provides better bondability with substrate, a good surface finish, and flexibility to the coated product.

To improve the processing properties of butyl rubber (IIR), the use of factices, stearic acid, and Shellflex790 (paraffinic hydrocarbon oil, Shell Chemicals) assists in the incorporation of fillers during compounding. In the calendering operation, these can control the dimensional stability of the coated material by maintaining an accurate gauge thickness of the rubber matrix.

EPDM elastomers with high ethylene content show good thermoplastic characteristics. These rubbers provide high green strength, and have very high Mooney viscosities at room temperature. However, at the processing temperature they exhibit normal processing behaviour for mixing and calendering.

Appropriate blending of high-ethylene content EPDM with broad molecular weight distribution grades helps to incorporate the reinforcing and non-reinforcing fillers in mixes with the addition of process oils for dispersion. In coating applications, good calendering can be accomplished at elevated temperatures [2].

High-ethylene content EPDM can also accept very high filler and oil loadings, and lower Mooney viscosity grades require lower amounts of plasticisers. Blends of EPDM and NBR can also achieve oil-resistant proofing at a lower cost.

For improvement in the processing of EPDM-rubber based compounds, use of naphthenic mineral oils is recommended; for high-temperature applications, paraffinic oil is recommended. Lack of appropriate tack of this elastomer compound causes adhesion problems. Hence, the use of appropriate tackifiers are particularly recommended for EPDM rubbers. They contribute to the improvement of adhesion and building tack.

EPDM rubber stocks mixed with very low molecular weight polymers, for example polymeric oils and Struktol WB 212 (a mixture of fatty acid esters), improve processing characteristics which give a better finish in proofing textiles. In promoting the tack of the compound for coating applications and building processes, CI resins and petroleum resins are suitable.

A conventional rubber-spreading machine is used for the spread coating of EPDM mixes. This is achieved by preparing a solution of correct viscosity in xylene/toluene solvent. Application of a very thin coating on the fabric is possible in this process. It can also be used in implementing an anchor coat for subsequent high-thickness coating if strong adhesion with the substrate is essential.

Silicone rubber gums compounded with fillers, processing aids, and curing agents can be processed on standard rubber equipment. Fine-particle silica fillers are used as reinforcing agents. They increase hardness, and can reduce stickiness on the mixing mill during mixing and in the calender rolls.

Silicone fluid of high molecular weight can be added in the compound as a plasticiser. A small proportion of polytetrafluoroethylene powder in the mix improves calendering. The compounded silicone rubber can be dispersed in suitable solvents, and a solution can be prepared in a 'Z' blade dough mixer. Dispersion coating of silicone rubbers on textiles using a transfer roll system or a rubber spreading machine gives thorough penetration of the solution into the fabric. This results in improved flexing properties and uniform electrical properties of the coated materials.

A solvent-dispersed mix of this elastomer can be coated on fabrics in a conventional rubber-spreading machine. Low viscosity silicone polymer compounds that do not contain solvents are also available as pastes. These may be used for spread coating and can be cured in the normal way; vulcanised silicone polymers are used for dip coating. Textiles can be coated by a knife on roll equipment or in a rubber-spreading machine.

In the dry system of coating fabrics with silicone rubber compounds in a 3/4 roll variable-speed calender machine, coating can be undertaken on one or both sides at a time. To obtain good polymer-coating behaviour and an excellent surface appearance, the speed of the rolls, and the roll temperature should be adjusted correctly. Good calendering is achievable by 'freshening' the compound before calendering. Maintenance of the temperature of the top roll at 50 °C, the centre roll at room temperature, and the bottom roll at a cool temperature can give satisfactory results [14].



For stocks prepared from Hypalon (chlorosulfonated polyethylene; CSM) rubber, it is necessary to uniformly warm-up the mix before calendering to obtain uniformity in the gauge thickness of the coated film as well as to avoid surface roughness. This polymer is thermoplastic, so breakdown during mill mixing is not necessary. Processing should be conducted at lower temperatures to prevent excessive softening. Mixes of chlorosulfonated polyethylene (CSM) containing reinforcing fillers with suitable lubricants can provide good calendering [12].

Calendering can be conducted in the temperature range 60-90 °C. To obtain a satisfactory surface finish during coating, release agents such as waxes/stearic acid or low molecular weight polyethylene may be added.

Coated textiles of CSM in an unvulcanised state may be warmed up on 'hot plates' to facilitate adhesion during build-up of the article. Specific grades of CSM polymer (e.g., Hypalon 30) mixes can be dispersed in organic solvents, and the textile fabrics coated in a spreading machine. This polymer has excellent colour stability and weatherability, so a wide range of brightly coloured coatings is possible if utilising the wet system of coating.

During the processing of a polysulfide elastomer, it does not breakdown to a desirable plasticity in the mixing mill. Certain amounts of benzothiazyl disulfide (MBTS) and diphenyl guanidine (DPG) can act as chemical plasticisers. These help to reduce the plasticity of this elastomer by reducing the molecular weight.

Mixing can be conducted in an open rubber mill or in an internal mixer at 54-71 °C. To obtain a satisfactory dispersion, the compounding ingredients should be added slowly at the early stages of mixing. To obtain adequate strength, 40-60 phr of semi-reinforcing or FEF blacks must be added in the mixes. The necessary tack may be promoted in the mixes by adding CR-W-grade rubber and CI resin. In combination with MBTS and DPG, the use of factices in the compounding provides satisfactory processing for coating in calenders. The processing characteristics and mechanical properties of this polymer are poor, and the odour evolved during processing may not be acceptable to the processors. Vulcanisation of formic acid (FA)-type polymers can be accomplished by incorporating zinc oxide in the compound. This removes the effect of the chemical plasticiser, and increases the hardness of the rubber [9].

The uncured polysulfide rubber-based compound can be dissolved in ethylene dichloride solvent, and the resulting cement applied for coating on fabrics in a rubber-spreading machine.

Polyacrylic rubbers of the ethyl acrylate type can be directly dissolved in solvents such as methyl ethyl ketone or acetone without treatment in a mixing mill or compounding.

They can be utilised for coating fabrics in a spreading machine. An extremely thin coating can be applied on a very lightweight natural fabric or man-made fabric using this method [5].

### **3.1.2 Adhesion to Fabrics**

The adhesion between the rubber matrix and the reinforcement material (e.g., natural/man-made woven, non-woven fabrics, cords, glass fibres or steel cords) must maintain an adequate strength between the rubber layer and the substrate according to the specified standards. The strength of bonding of the textile with the rubber matrix is dependent upon the nature of the polymer, its inherited tackiness, nature of the fabric, and constructional factors. Textiles having protruding fibre ends with high individual strength can provide very good adhesion strength mechanically. The significant criterion of bonding to fabrics with rubber is to prevent the rubber coating from separating out during service on high flexing applications and if used in high dynamic stresses.

To promote adhesion between rubber textile interfaces (particularly with man-made fabrics, and cords) the fabric must be specially treated. A widely used method is the dipping process in the resorcinol-formaldehyde-latex (RFL) mix.

Fillers increase the adhesion level by enhancing the modulus and tear strength of the compound. A high modulus of the vulcanised matrix of the coated textile can reduce the difference in extensibility between the textile substrate and the rubber film. This reduces the strain at the separating point, and high tear strength prevents the rubber coating being stripped out from the substrate [10]. A simple rubber textile adhesion test is shown in **Figure 3.1**.

Reinforcing silica fillers increase the physical properties, modulus and tear strength of the compound and improve the adhesion strength. Non-reinforcing inert fillers do not reinforce the mixes, and do not significantly increase the tear resistance. A higher level of tensile strength, modulus, and tear strength can be achieved by incorporating the reinforcing carbon blacks in to the stocks. High tensile strength mixes provide relatively better adhesion with the substrate.

Some special additives may also be incorporated directly into the compound to promote bonding to the fabric. These include reactive resins, and a resorcinol-formaldehyde silica combination in the form of a dry bonding agent. Special treatment is usually not required for natural fibres such as cotton, wherein mechanical anchoring with loose fibre ends may give the desired result. It is also general practice in the coating industry to use the in-house adhesive system for bonding to continuous filament textile

materials if a high specified limit of bond strength is required for special applications of the coated textiles.

To promote the tack of the rubber compounds utilised to produce coated fabrics, the addition of pine tar, rosins, CI resins and other hydrocarbon resins can help to promote tack in the uncured state. This helps in the fabrication of coated materials in the building up of ply-to-ply construction of tyres, conveyor belts, flat transmission belts, hoses, insertion sheets, and footwear, etc.

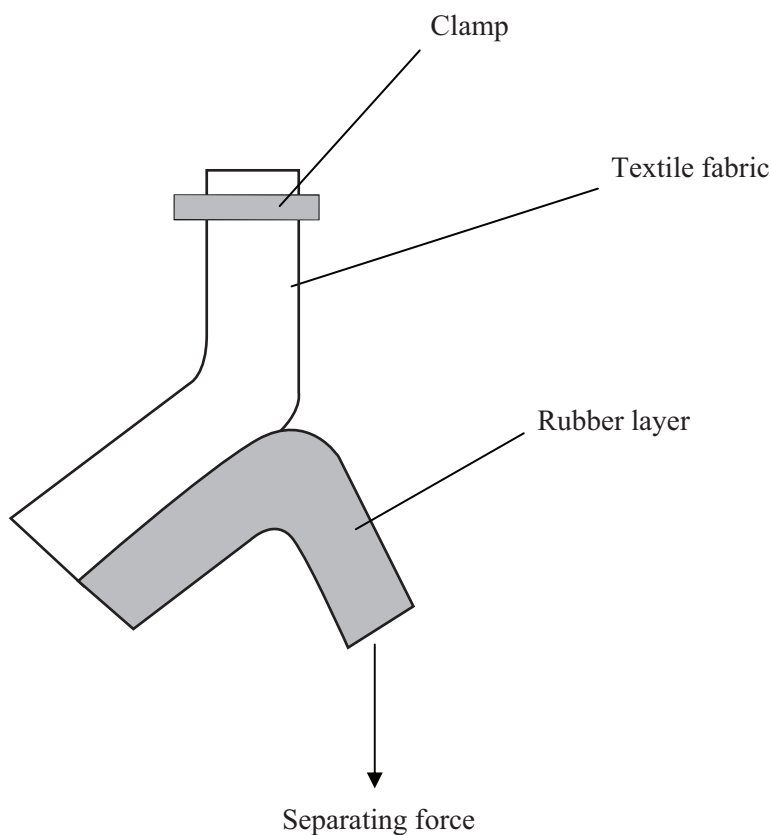
The benefit of the addition of resins into the mixes is to increase adhesion strength by spreading the stress over a wider surface area, thereby promoting adherence with the substrate by mechanical action. During vulcanisation, crosslinking takes place between the rubber coating and the resin, resulting in the increase of bond strength between the rubber and textile/cord substrate [11].

Polymer selection is dependent upon the adherence characteristics during coating to achieve the best parameters in the final coated product with respect to bondability. However, the final bonding property with the substrates and rubber layer is obtained on appropriate vulcanisation of the coated material. The curing agent has a marked effect on adhesion properties. For example, reduction of the amount of sulfur in the compound reduces the adhesion strength considerably if a sulfur cure system is used. A curing system designed without the addition of free sulfur results in extremely low adhesion strength.

Suitably compounded unsaturated hydrocarbon polymers such as NR and SBR impart satisfactory adhesion with textiles. The correct choice of fillers (particularly reinforcing fillers) in the correct proportion and the incorporation of tackifying agents (e.g., resins) produce good results. Addition of a larger amount of zinc oxide (10 phr) enhances the tack of the compound (particularly in NR), and can retain the tack for a very long period of time in the unvulcanised state. This property is exploited in rubber-coated adhesive tapes in the uncured state, which are used for surgical dressings.

Satisfactory adhesion levels can also be achieved by using unsaturated hydrocarbons such as polyisoprene and PBR. If the strength of adhesion is measured, SBR confers a marginally higher adhesion strength in comparison with NR-based stocks.

Bonding with substrates shows the best results if polar backbone polymers such as CR and nitrile rubbers are used for coating. Highly saturated elastomers such as butyl elastomers and EPDM have no tack for adherence with the substrate. They need tackifiers or special additives to promote tack to obtain adhesion with the textile bases.



**Figure 3.1** Adhesion test of a rubber-coated textile (schematic)

However, the bond strength obtained is at a considerably lower level. In such situations, blending of tackifying elastomers in small proportions with these rubbers may offer good results. Substrates treated with suitable chemical bonding agents or using dry bonding agents directly into the mixes (resorcinol formaldehyde donor with reinforcing silica) provide higher adhesion strengths.

The factors responsible for adhesion between rubber textiles interface are:

- Mechanical adhesion.
- Formation of primary and secondary chemical bonds.
- Diffusion of adhesive components into the internal structure of the fibres.

It is always preferable to apply the adhesive coating in a fluid process system to achieve the optimal adhesion.

Special-purpose synthetic elastomers such as CR- and NBR-based compounds give satisfactory adhesion if RFL–vinylpyridine (VP)-butadiene-styrene terpolymer latex-dipped continuous filament fabrics are used for coating. Improvement in adhesion level can also be achieved using CR and NBR lattices by replacing VP latex.

In the case of IIR-based coating applications, a chloroprene-based latex RFL system can offer the desired bonding properties.

Chlorosulfonated polyethylene (Hypalon 20) and EPDM rubber exhibit very poor tack. This causes difficulties in coating applications; inclusion of ~20% of NR into the compound as a tackifier can provide satisfactory adhesion [7].

It may also be applied on RFL-treated man-made textiles without having a major effect on the properties (e.g., weathering and ageing) of base rubbers. To promote better adhesion of silicone rubber-based compounds on various textile substrates, the addition of silane coupling agents to the compound produces the best results.

Several proprietary/branded liquid bonding agents such as Chemlok (Hughson Chems) and polyisocyanate in methylene chloride are available for obtaining successful bond strengths with man-made/synthetic textile substrates with different rubbers. These type of liquid bonding agents are, in general, applied as a ‘base coating’. This is a mixture of compounded rubber solution prepared in solvent to which is added 10–15% of a liquid chemical bonding agent on the untreated synthetic textile surface before the application of coatings in a spreading system or calendering process.

The best results are achievable by using the compounds in solution form; these can be applied as coatings on a rubber-spreading machine. This may be followed by dry application of the subsequent coating in a calendering machine. This is particularly applicable for special-purpose synthetic rubber coatings on synthetic textiles [6].

### **3.2 Requirements of Physical and Chemical Characteristics**

When using carbon black, the primary importance in general rubber compounds is to reinforce mechanical properties such as tensile strength, modulus, and tear resistance. In textile coating applications, moderate mechanical properties may be required for industrial uses. The appropriate grade of carbon black required to achieve specific physical and processing properties is shown in **Table 3.1**.

Table 3.1 Types of Carbon Black used for textile coatings				
Type of Carbon black	ASTM designation	Particle Size (nm)	DBP absorption	Iodine number
General Purpose Furnace (GPF)	N 660	49-60	90	36
Semi Reinforcing Furnace (SRF)	N 762	61-100	65	27
Fast Extrusion Furnace (FEF)	N 550	40-48	121	43
High Abrasion Furnace (HAF)	N 330	26-30	103	82
Intermediate Super Abrasion Furnace (ISAF)	N 220	20-25	114	121
<p>ASTM D 1765 - detailed the nomenclature for carbon black.</p> <p><b>DBP absorption</b> – measurement of the structure of carbon black aggregate, DBP in cc absorbed by 100 gm of carbon black. Higher the DBP number, higher the structure.</p> <p><b>Iodine number</b> – iodine in gm absorbed per kg of carbon black, higher the number smaller the particle.</p>				

Improvement in physical properties takes place as the carbon black aggregates and makes physical and chemical bonds with the rubber. This enhances the tensile strength, tear strength, abrasion resistance and flex fatigue resistance.

Coated textiles must be pliable, soft and resilient if utilised for the production of waterproof garments, bedspreads, hospital sheeting, air pillows, air beds, and water beds.

For white, off-white and coloured fabric coatings, use of lower particle size precipitated silica in the mixes as a reinforcing filler enhances mechanical properties such as tensile strength, tear and abrasion. Aluminium and calcium silicates, as well as stearic acid-coated calcium carbonate ('activated calcium carbonate') can also offer the desired result. Silica exhibits higher reinforcement in polar elastomers such as CR and NBR. In NR- and SBR-based compounds, reinforcement is improved by using a saline coupling agent along with silica. It can also contribute to tear, cut, and chipping

resistance, and lowers heat build-up characteristics in high flex uses. The average surface area of silica is 152 m<sup>2</sup>/g [7].

The smaller particle size carbon blacks cover a higher surface area which helps to increase the mechanical properties of the elastomer. The viscosity of the compound, hardness, calendering shrinkage, thermal and electrical conductivity, permeability parameter of the liquid and gas are also affected by the percentage of black in the mixes and are also dependent on the structure of the blacks used. Usually 5-10 phr of carbon blacks are used for black pigmentation; a higher amount improves mechanical properties. Using higher structure carbon blacks in the mixes will help to reduce the shrinkage problem, and also helps to improve the surface smoothness in the calendering operation. The processing temperature increases with an increasing structure level. Also the rate of calendering decreases when the surface area of carbon black used in the mixes is increased.

To obtain good dimensional stability of the calendered material and to achieve a good surface, excellent dispersion of blacks into the compound is necessary.

The electrical property of rubber fabric-coated material is highly dependent upon the design of the compound and the manufacturing process. NR-based items can offer high voltage insulation if the thickness of the rubber matrix on the textile substrate to be considered for electrical insulation applications.

Rubber-coated fabrics may need to be flame resistant in many domestic and industrial applications such as carpet backing, waterproof roofing, and for conveyor belts used in mines. This property can be further enhanced by incorporating flame-retardant additives.

Incorporation of rubber-blowing agents as compounding ingredients give a sponge rubber lining which decomposed during vulcanisation.

Coated textile materials used on outdoor and underground areas may be infested with fungus and insects; these are sometimes attacked by rodents. Rodenticides and bacteriacides may be added as compounding ingredients to prevent possible damage by rodents and micro-organisms.

Pleasant-odoured substances may be required for certain rubber-coated fabrics used for domestic articles/hospital bedspreads to mask the smell of the basic rubber or if a pleasant smell is demanded by the user. In such cases, flavouring agents may be incorporated in the mixes.

**3.2.1 Tear and Abrasion Resistance**

‘Resistance to tear’ can be defined as the resistance to cut growth in a polymer under an applied tension. The resistance to rubbing in service can be explained as the abrasion resistance to the rubber-coated surface. The test for abrasion resistance of a test specimen in the laboratory may not have relevance in relation to the actual service life of the coated material. It is difficult to measure the actual use under service conditions [10].

Resistance to abrasion of a compounded elastomer used as coating fabric can give poor results due to insufficient crosslinking or vulcanisation; the elastomer can also deteriorate considerably if the crosslinking is excessive. The highest value of tear resistance can be obtained on a slightly lower degree of cure, and can decrease rapidly on the onset of over-curing. In an atmosphere of increasing temperature, the tear resistance will decrease. In NR, SBR and CR compounds, reducing the particle size of reinforcing fillers such as high abrasion furnace, intermediate super abrasion furnace, and super abrasion furnace grades of carbon blacks can offer higher abrasion resistance [1]. For non-black compounds, the use of very low particle size silica (precipitated/fumed silica) gives higher abrasion resistance to the cured rubber in comparison with other active fillers. The use of different types of carbon black in textile coating formulations to acquire processing advantages, high abrasion, and high tear are detailed in Table 3.1 and Table 3.2.

Table 3.2 Grading of carbon black on surface area parameter	
Type of carbon black	Surface area (Sq.mt/gm)
Semi reinforcing	< 45
Reinforcing	65 - 140

PBR shows higher abrasion resistance. Addition of a certain percentage of this rubber in a compound based on NR, SBR and CR can markedly enhance abrasion resistance. NR, being non-polar, can be readily blended with non-polar rubbers, and can contribute its excellent tear and abrasion resistance to the blends. This practice is widely followed in the rubber industry, and this is advantageous specifically for coating applications [13].



NR exhibits good abrasion and tear resistance. Incorporation of reinforcing fillers in the compounds of NR further improves the abrasion and tear resistance as well as tensile properties, but the fillers also reduce the rebound of elasticity.

It is necessary to increase the physical properties of SBR compounds by using reinforcing fillers. To enhance the tear resistance of this elastomer, carbon black at the optimum level may be necessary, but this is not achievable up to the level of NR. If formulated with reinforcing fillers in a correct proportion, SBR compounds can offer abrasion resistance comparable with that of NR.

In comparison with NR, SBR exhibit better crack initiation and abrasion resistance than NR. PBR have excellent abrasion resistance and can also be blended with NR and other synthetic rubbers to improve this property.

Appropriate curing of the elastomer plays a greater part in abrasion resistance. This property may deteriorate if crosslinking is insufficient.

Coumarone resin, petroleum, and phenolic resins, if added in the correct proportion (~5 phr), provide improvements in tear resistance. In combination with white reinforcing fillers, resins can effectively help in wetting of the surface of reinforcing fillers, thereby offering better incorporation of fillers in the elastomer mixes. This will exhibit improved tear and abrasion resistance of the resultant white/coloured mixes of NR and synthetic rubber-based elastomers. The abrasion resistance of NBR lacking reinforcing fillers is low. However, if compounded with reinforcing fillers, this property is greatly increased, and can reach the level seen in NR and SBR.

Carboxylated nitrile and hydrogenated nitrile rubbers containing one or more acrylic type of acid terpolymer are available. They can offer extremely high abrasion resistance and excellent tear resistance to the resultant compound.

Improvement in the mechanical properties of EPDM rubbers are dependent upon the type and percentage of fillers used in the formulation. At high temperatures, tear resistance is comparable with the level of NR. Good-to-excellent abrasion resistance of this polymer is also achievable (similar to that of NR).

The abrasion and tear resistance of IIR shows moderate-to-good performances if used in coating applications.

In comparison with many other elastomers, the abrasion resistance and tear resistance of silicone rubbers are poor-to-fair. However, at higher temperatures, these properties are virtually unaffected [14].

### **3.2.2 Resilience and Flexibility**

Fabrics used for rubber coating should provide the desired elongation and flexibility in relation to the extensibility of the rubber to prevent the rubber layer separating out of the substrate. The resilience of rubber and heat build-up can be stated as the ratio of return to effected energy. The heat generated is the measurement of the amount of energy absorbed that is impacted.

Resilience can be improved with the structure of the vulcanised rubber by increasing the crosslink density, but can deteriorate if there is excessive crosslinking. The rebound resilience at elevated temperatures influences a higher degree of crosslinking, but this property shows a minimum level on a slight excess of crosslinking. During cyclic deformation of the sample, heat build-up is primarily dependent upon the chemical structure of the polymer and the nature of crosslink formed.

Among the commonly used commercial rubbers, NR, SBR and chloroprene rubbers exhibit high resilience and flexibility. Polybutadiene elastomers have the highest resilience, and butyl rubbers the lowest. Increasing the resilience of the elastomer is dependent upon the butadiene/isoprene ratio of the polymer. Copolymers of SBR, NBR and isobutylene are common examples.

A polysulfidic network and slight modification of the main chain can provide high resilience. Low sulfur-cured nitrile rubber-based compounds show the higher heat build-up when compared with NR. Resistance to fatigue of the compounded elastomer is primarily dependent upon the ratio of sulfur to accelerator concentration, modification of the cured rubber main chain, and the type of crosslinking.

Vulcanisation is a complex phenomenon. Crosslinking may be of mono, di-, tri- or higher polysulfides. The efficiency and rate of cure is increased by the use of rubber accelerators if sulfur is added as the crosslinking agent; the time and temperature are also important factors. Good physical properties such as tensile strength, tear, fatigue, and excellent low temperature crystallisation resistance are obtainable with the polysulfide network. There is deterioration in the elongation at break with an increasing degree of crosslinking, but a higher value can be obtained at a lower degree of crosslinking.

Resilience progressively decreases with the loading of low particle size reinforcing fillers such as carbon black or silica. With an increasing quantity of fillers, the resilience decreases in elastomers such as NR and CR. High resistance to flex-cracking can be obtained in CR-based compounds which may be further enhanced if they are formulated with protective agents [10].

Cured chloroprene rubbers exhibit good resilience. This is dependent upon the design of the compound and appropriate use of synthetic plasticisers in the stocks. The addition of ester plasticisers in nitrile rubber compounds can also increase the resilience considerably.

The most commonly used processing aid (particularly in calendering mixes), factices, is to be avoided if high-resilience stock is needed.

Depending on the acrylonitrile content of the polymer, the rebound resilience of nitrile rubber is lower than that of NR, SBR and CR. However, this property can be enhanced by using rubber with lower acrylonitrile content. The resilience of NBR is also influenced by the formulation, choice of fillers, incorporation of synthetic plasticisers, and the curing system. Butyl rubber shows low rebound resilience but its brittleness temperature is very low ( $-75^{\circ}\text{C}$ ).

Polyolefin elastomers are highly resilient, and their rebound resilience is close to that of NR. Commercially available low molecular weight liquid nitrile can be used as a plasticiser in NBR compounds with low or no extractability. This can be partially crosslinked to the main chain during cure, and offers good resilience and flexibility to the elastomer. The heat build-up of NBR compounds is more upon flexing if cured with a low sulfur-content system than that of NR with a similar system.

The resilience of EPDM polymers and rebound resilience are excellent, having relevance with NR in the low temperature range of  $-40^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ . The elasticity of EPDM elastomers is also higher when compared with several synthetic rubbers, but to a lesser extent with NR, whereas the flexibility at low temperature can be compared with that of NR [15].

Silicone polymers provide good flexing properties if the coated textiles made of these elastomers are used in flexing zones at various temperatures.

### ***3.2.3 Characteristics of Environmental Resistance: Ozone and Ultraviolet Light***

Cracking on the surface of the coating is observed if rubber-coated fabrics are subjected to stretch under dynamic conditions. This phenomenon may differ from the type of polymer used and the design of the recipe of the compound used for coating. Ozone in the environment, even at very low concentrations, is responsible for this effect. The degree of resistance to ozone attack is dependent upon the type of polymer. This is lowest for NR and SBR and highest for EPDM. The inherent properties of polyacrylic

elastomers with respect to ozone- and weather-resistance mean that protective agents may not be needed in most cases.

The ozone resistance of any rubber can be improved by using antiozonants of *p*-phenylenediamine and or by incorporating waxes in the rubber mixes. Waxes, because of their limited compatibility, will bloom on the surface and offer a protective layer. However, in high-flex conditions, the surface layer may develop cracking and will not serve its purpose. If there is tendency of blooming to the surface, this may also affect the adhesion characteristics with the fabric and the rubber coating.

When the coated fabric is exposed to the weather, a combined effect of atmospheric ozone, temperature, ultraviolet (UV) light, dust erosion, rain, and snow may cause deleterious effects on the rubber matrix. If the coating is exposed to direct sunlight, it gives rise to considerable heat build-up. In black compounds the rate of heat build-up is higher; it is minimal in white and intermediate-coloured compounds. Inclusion of a higher amount of zinc oxide (~10 phr) can help to improve heat resistance, and will act as a stabiliser for white/colour-coated articles upon absorbing UV rays if the material has been exposed to direct sunlight for a long time.

In such applications, the choice of the basic polymer, selection of fillers, and use of a protective agent are the important factors for compound design. The colour of the coating may affect enhancement of the surface temperature if exposed to the weather.

Upon exposure to UV light or direct sunlight, the ingredients of the coating compound must be carefully selected. The ingredients should be able to reflect UV light (or be able to absorb and transform it into harmless wavelengths if necessary). In the filler system of the compound, incorporation of white fillers such as calcium carbonate and barium sulfate in coloured/white coating compositions can offer good UV reflectance, and fine-particle carbon blacks are effective in absorbing UV light.

The unsaturated part of a rubber molecule available for sulfur vulcanisation is susceptible to attack by oxygen, ozone, heat, light, metal catalysis, and flexing.

Compounds based on NR, SBR, PBR, NBR and CR contain an unsaturated group, free double bonds, and uncombined sulfur after vulcanisation. Attack by oxidation and degradative agents such as ozone are initiated on those sites. Silicone rubber-based compounds do not need protective agents because they are extremely ozone-resistant. Two main classes of chemical are administered to inhibit the degradation process of unsaturated rubbers: amines and phenolics. The former are staining and the latter are not [2].

Appropriate selection of protective agents is very important. Incorporation of antioxidants such as polymerised trimethyl dihydroquinoline in NR and synthetic

rubber mixes used for coating can protect against oxidation and heat under severe conditions. This antioxidant is moderately staining and can be used in coloured coating compounds if slight discolouration of the mix is acceptable. In most of the rubbers, it also improves the ozone resistance to some extent [12].

To achieve resistance against flex cracking, heat and oxidation, the suitable antioxidant is diphenylamine-acetone in a liquid form. Excellent flex cracking and ageing resistance can be provided by the use of diphenyl-*p*-phenylene-diamine (Nonox DPPD-ICI) in CR-based compounds; DPPD improves ozone resistance.

To protect natural rubber, polyisoprene and chloroprene from deteriorating in the presence of copper and manganese, di-*b*-naphthyl-*p*-phenylenediamine (Agrite white – Vanderbilt) is a suitable antioxidant and also gives protection against oxidation and heat.

Nickel diisobutyldithiocarbamate is a suitable antioxidant for SBR and CSM polymers. In peroxide-cured ethylene propylene and EPDM elastomer-based compounds, further protection can be provided by using nickel dimethyldithiocarbamate as an antioxidant.

For non-staining and non-discolouring NR and synthetic rubber-based compounds, phenolic-type antioxidants (Nonox WSP, ICI), and styrenated phenols (Nonox SP, ICI) are suitable antioxidants in the compound mixes for calendering and spread-coating applications. Protection against photo-oxidation of light coloured-coated articles if exposed to light can be achieved by adding phenolic antioxidants with a UV absorber such as a benzotriazole derivative (Tinuvin P, Ciba Geigy) [6].

The selection of mercaptobenzimidazole (Antioxidant MB, Bayer) as a non-staining antioxidant for white and lightly coloured coating compounds can offer excellent protection against metal contamination. It provides synergistic results if used in combination with phenolic antioxidants in NR and synthetic rubber compounds.

Moderate protection from atmospheric cracking and sunlight can be provided by using paraffin wax in the compound in excess (2 phr). This may bloom to the surface after vulcanisation and can offer a protective layer. However, the layer may crack if subjected to stress. In such cases, microcrystalline waxes give the desired result. Care must be taken regarding the adhesion criteria with the fabric substrates when waxes are incorporated in the formulation in excess because of its blooming.

### **3.2.4 Low Temperature Flexibility of Elastomers**

All elastomers become stiffer and ultimately unusable on progressive cooling. This adversely affects the function of a rubber-coated textile material, and severe cracking may occur on flexing. A viscous rubbery material becomes stiff and brittle at a temperature or range of temperatures: this is the glass transition temperature ( $T_g$ ) [5].

Conversely, an elastomer behaves like a viscous material as the temperature increases. The level of temperature varies from rubber to rubber. Low temperature brittleness or the  $T_g$  is the measurement of the temperature limit to a rubbery state; it is an important property for classifying an elastomer.

Rubbers used in coated textiles for low temperature applications should have a low  $T_g$ . In some cases, coating compounds can be formulated with suitable compatible plasticisers, and paraffinic process oil may be used if needed. These can lower the  $T_g$  of the resultant mixes for use in the coating.

Stiffening of the elastomer occurs if it is exposed to the environment at low temperatures. This is seen in high-gum-strength rubbers which crystallise upon stretching (e.g., NR and CR). In NR, the stiffening starts rapidly at  $-26\text{ }^{\circ}\text{C}$ , but the  $T_g$  of this rubber is as low as  $-75\text{ }^{\circ}\text{C}$ . Cracking of the coating will occur during stiffening in NR-based compound-coated fabrics at dynamic conditions.

The low temperature behaviour of rubbers can be improved by incorporation of compounding ingredients such as fillers, and by using higher amounts of plasticisers in the mixes. This property can also be improved at a higher degree of crosslinking of rubbers [16].

In CR, the stiffening occurs at  $-12\text{ }^{\circ}\text{C}$ , but the flexibility of CR can be achieved up to  $-50\text{ }^{\circ}\text{C}$  by the addition of aromatic mineral oil into the compound. The crystallisation temperature of the coating compounds can be minimised with very tight crosslinking, incorporation of a high proportion of fillers, and use of petroleum-based plasticisers.

Compatible plasticisers having the lowest freezing point (e.g., adipates, sebacates, paraffinic process oils, butyl oleate) may be used in the compounding to minimise low temperature flexibility. In CR compounds, ester plasticisers should be avoided because they may increase the rate of crystallisation.

For NBR, grades with low acrylonitrile content should be used. Further improvement is possible while designing formulations for coating by using suitable synthetic plasticisers in the mixes, which can accomplish low temperature flexibility at  $-22\text{ }^{\circ}\text{C}$ . The effective plasticisers are thioether esters to improve the low temperature flexibility of NBR as well as CR.

The low temperature characteristic at the lowest range is available in silicone rubbers. They remain flexible at  $-100\text{ }^{\circ}\text{C}$  (the lowest level is  $-120\text{ }^{\circ}\text{C}$ ). These rubbers do not require plasticisers (as is the case for other elastomers).

The brittle point of IIR is  $-75\text{ }^{\circ}\text{C}$ . The low temperature flexibility of this polymer can be improved by adding low-volatile, high molecular weight esters. Very good low temperature flexibility is an inherent property of EPDM rubbers ( $-58\text{ }^{\circ}\text{C}$ ) and they can retain dynamic properties at a low temperature range better than SBR and IIR. The dynamic properties in the low temperature range of EPDM can be compared with those of NR.

PBR have excellent low temperature properties and the  $T_g$  is as low as  $-90\text{ }^{\circ}\text{C}$ . They remain flexible at wide range of low temperatures. Some of the grades of polyacrylic rubbers can be used at  $-30\text{ }^{\circ}\text{C}$ ; they can be used as low as  $-40\text{ }^{\circ}\text{C}$  by adding appropriate amounts of special plasticisers from the thioether and adipate groups [17].

### **3.2.5 Electrical Conductivity and Electrical Resistivity**

Volume resistivity is the resistance offered between opposite faces of the rubber on the application of electric stress - it is measured in ohm cm. Measuring the insulation property of rubber mixes and the dielectric strength is important. Dielectric strength is the difference in voltage per unit thickness at which electrical breakdown occurs, or the resistance offered at each centimetre of thickness of the rubber. Applying maximum voltage to a material without causing its breakdown is expressed in volts per cm [19].

Electrical properties are dependent upon the selection of polymers, choice of compounding ingredients, and the overall vulcanisation system of the rubberised textiles. If coated fabrics are used for electrical resistance purposes (e.g., covering of electrical installations or in conductive/anti-static applications), the electrical characteristics of the rubber compounds must be carefully considered.

Rubberised fabrics are utilised in the making of electrical resistant/anti-static footwear, anti-static belting, hoses, and aprons for surgeons. They may protect the final product from direct electrical shock or shock from static charges [18]. Dielectric strength is an important characteristic in the choice of rubbers used for electrical resistance-coating or for anti-static purposes.

NR- and SBR-based coatings can provide good dielectric properties. If formulated appropriately, CR and NBR can offer good insulation when used in low-voltage areas. Insulation properties may increase with the degree of crosslinking, and reduced water absorption of the compound, which can be used for the insulated

product. The electrical insulation properties of different rubbers are shown in Table 3.3.

Table 3.3 Electrical insulation properties of various elastomers	
Elastomers	Properties
Natural rubber	Excellent
Polybutadiene rubber	Excellent
Styrene butadiene rubber	Very good
Nitrile rubber	Fair
Polychloroprene rubber	Fair
EPDM rubber	Excellent
Silicone rubber	Excellent

NBR are not particularly suitable for electrical insulation applications. However, the designing of excellent anti-static compounds is possible if suitably formulated mixes are made by selecting high acrylonitrile-grade polymers. Incorporation of anti-static plasticisers and conductive grades of carbon blacks into the mixes can further increase the anti-static properties of NBR.

The electrical properties of coating compounds are not only dependent upon the correct choice of elastomers, but also on the level and nature of fillers and plasticisers used. Selection of fillers, resins and plasticisers are the most important criteria to obtain appropriate electrical characteristics. Fillers such as talc, hard clay, coated silica, whittings, and calcined clay give high insulation, ensuring resistance while the coated material is immersed in water.

Mineral fillers having low water-soluble characteristics offer higher electrical resistance and dielectric properties in comparison with carbon black. Specific types of carbon blacks such as conductive channel, super-conductive furnace blacks, and acetylene black increase the electrical conductivity if used in an anti-static rubber layer. The volume resistivity of such coating layers should be maintained at  $10^2$ - $10^{10} \Omega \text{ cm}$  to achieve good anti-static properties.

Addition of chemical anti-static agents such as ethylene oxide condensate into the mixes used for coatings reduces the electrical resistance to a level at which static electric



charge is dissipated. While processing, the static charges may also accumulate due to frictional electricity generated during spread coating. It is an acceptable practice in the rubber-coating industry to add chemical antistatic agents directly to the rubber solution to avoid fire hazards due to accumulation of static charges in the spreading machine, where a large amount of highly inflammable solvents are usually employed to prepare the rubber dough.

Table 3.4 Volume resistivity and dielectric strength of different rubbers		
Rubber	Volume resistivity at 20° C ( $\Omega$ cm)	Dielectric strength at 20°C (kV/cm)
Natural rubber	$10^{15}$	210
Styrene butadiene rubber	$10^{15}$	190
Polychloprene rubber	$10^{12}$	225
Nitrile rubber	$10^{10}$	165
Butyl rubber	$10^{16}$	250
EPDM rubber	$10^{16}$	350
Silicone rubber	$10^{17}$	200

To achieve excellent anti-static properties of the rubber matrix, ethylene oxide condensate (5 phr) in addition to aluminium silicate as filler can be incorporated in the compound based on elastomers such as NR, CR and NBR.

A test procedure of surface and volume resistivity is given in BS 903 Part 33 [19]. The volume resistivity is categorised according to the following parameters: (i)  $\leq 10^4 \Omega$  cm is conductive; (ii)  $10^4 \Omega$  cm and  $10^8 \Omega$  cm is anti-static; and (iii)  $\geq 10^8 \Omega$  cm is insulating.

For coloured coating mixes, the use of coated silicas with low water-soluble contents results in higher electrical resistance and dielectric characteristics than that seen for furnace blacks. To obtain anti-static products, the incorporation of synthetic aluminium silicates filler can give satisfactory results.

For the selection of processing aids, petroleum oils with high volume resistivity ( $\sim 10^{13} \Omega \text{ cm}$ ), such as paraffinic oils, offer a higher resistance than the aromatic and naphthenic types. Plasticisers such as dioctyl phthalate and dioctyl sebacate have a resistivity of  $10^{11} \Omega \text{ cm}$ , whereas phosphate plasticisers have values as low as  $10^8 \Omega \text{ cm}$ .

High resistivity can be achieved with low water extracts of NR and SBR, but this property can also be provided with IIR-based compounds [2].

Rubber compounds used for coating fabrics must have minimal water absorption to maintain good electrical resistance during service. CR, CSM and nitrile butadiene rubber-polyvinyl chloride (NBR-PVC) blends are most suitable for outer protective coatings over the insulation layer if weather- or solvent-resistance is necessary. The electrical properties of some rubbers are given in **Table 3.4**.

### **3.2.6 Impermeability to Air and Gases**

Impermeability to air or gases through the polymer film on the textile substrate is an essential requirement for inflatable rubber items. The diffusion of gas molecules through the coating membrane in the molecular spaces of the polymer and the solubility of the gas in the elastomer both affect the impermeability of rubber-coated fabrics. When selecting the elastomer, these factors must be taken into consideration to enhance the air/gas retention of the coated rubber.

This property is particularly important if the rubberised fabrics are used for the construction of inflatable items in the unvulcanised form (subsequently cured in the fabricated form) and/or from cured fabrics. The rate of diffusion of gases through the coated membrane can also be lowered by increasing the crosslink density of the rubber. The volume difference or pressure on both sides of the polymer coating can be measured to assess the permeability factor of the elastomer.

NR and SBR show lower retention of air and gas. CR shows better impermeability in comparison to NR and SBR. When compared with NR or SBR, NBR-based compounds offer better impermeability. This property may increase with the use of higher acrylonitrile-content NBR, which is almost equal to the impermeability levels of butyl rubber (which has the highest retention). The degree of cure, as well as the amount and type of fillers added into the compound also affect the rate of gas/air diffusion [18].

Epoxidised natural rubber (ENR) produced by the epoxidation of NR latex shows improved resistance to air/gas permeability comparable with that of butyl rubber. Two grades of this new-generation elastomer, ENR-25 and ENR-50 have been produced.

Its application to fabric coating is yet to be established for use in rubber-coated inflatable materials. IIR-coated textiles provide exceptionally low permeability. They can provide at least eight-times higher air retention in comparison with NR-coated materials. The polyisobutylene portion and saturated chain of the butyl molecule provide a high degree of impermeability and solubility of gases [16].

This outstanding property is employed in butyl rubber-coated fabrics if extremely low or zero permeability of gases is required (especially when inflatable items are made for engineering and defence applications).

EPDM polymers offer good permeability resistance in comparison with the other polymers. However, they exhibit 15-20% less air permeability when compared with butyl rubber-coated materials.

Polysulfide rubber (FA grade) shows extremely low permeability to organic liquids, water vapour, and gases in comparison with NBR, CR and diisobutylene rubbers. Its high resistance in many solvents prevents vapour permeability through the membrane if the fabric is coated with this elastomer.

The solubility and rate of diffusion of gases of the coated rubber are dependent upon the amount of gas absorbed and the amount passed out of the elastomer as well as the rate of diffusion of the gas through the rubber layer.

In comparison with other polymers, silicone rubbers, because of the microporosity in their molecular structure, are highly permeable to gases or liquids while there is a difference in pressure and temperature. Permeability is many times higher in comparison with other polymers used for coating. It predominates if the coating membrane is thinner on air-permeable fabric substrates. This special property of silicone rubber is advantageous for the construction of several specific medical devices that utilise coated fabrics [14].

### **3.2.7 Resistance to Water, Acids and Alkalis**

Rubber-coated fabrics in major application areas must be highly waterproof. Also, in certain specific uses, they must also be resistant to acids/alkalis of different concentrations. To improve the water resistance of the coating, using water-soluble salts in the compound mixes should be avoided. The selection of elastomers, compounding ingredients, and choice of curatives play a major part in accomplishing resistance against water and chemicals containing hydroxyl groups.

NR- and SBR-based mixes are suitable for the use of polymers resistant to dilute acids and alkalis having a minimum oxidising affect. IIR and EPDM polymers have good resistance to oxidising chemicals. The degree of resistance to oxidising chemicals is dependent not only on the formulation of the mixes but also on the temperature and duration of exposure. CSM (Hypalon) is the correct choice for high resistance against chemicals (particularly against oxidising chemicals).

Polymers with a relatively inert backbone (e.g., IIR, CSM, EPDM) have outstanding resistance against chemicals, acids and alkalis. For high resistance against chemicals, addition of inert fillers such as hard clays and barytes (barium sulfate) offer very good resistance to acids in coloured coating mixes.

To improve the water resistance of the rubber coating, the use of water-soluble salts in the mixes should be avoided to prevent the ingress of water. Mineral fillers containing traces of soluble salts can also give low water resistance to the coating [5].

CR-based filler-loaded compounds used for coatings provide very good water resistance if formulated with magnesium oxide in combination with zinc oxide, reinforcing silicas, and talc (particularly for brightly coloured compounds).

When compounded with CR, the selection of the curing system and choice of fillers are important factors. A high resistance against water of CR mixes can be achieved with a high degree of crosslinking and very low content of electrolytes (e.g., acids, bases or salts).

The water resistance of non-loaded CR is inferior due to absorption of water by the polymer. In this respect it shows a comparatively lower value than that for NBR, PBR and SBR.

Trace amounts of soluble chlorides are found in CR compounds when they are cured with a magnesia-zinc oxide system. This can be avoided by preparation with a lead oxide cure system where maximum resistance to water is necessary because lead chloride has limited solubility in water. To increase the degree of water resistance of CR compounds (particularly if the service demands immersion of the coated product in water), inclusion of red lead or litharge in the formulation at 10-20 phr offers very good results.

Adding 0.5 phr of sulfur and 1 phr of tetramethyl thiuram monosulfide along with litharge increases the degree of crosslinking. This results in excellent water-resistance of the coating mixes based on this elastomer. In black compounds, carbon blacks, reinforcing silica, and inert filler combinations also improve the water-resistance of CR-based coating compounds. Hydrolysis-resistant ester plasticisers such as trioctyl

phthalate, compatible mineral oils, and chlorinated paraffins are the appropriate additives for high water resistance. Processing aids and mineral oils in addition to ester plasticisers are essential to obtain acid- and alkali-resistant coating mixes based on CR. This elastomer shows good resistance to dilute alkalis and acids, but its resistance to concentrated acids is very poor [2].

Butyl rubber imparts very good resistance to concentrated mineral acids for a longer duration because of its low degree of olefinic unsaturation in the saturated hydrocarbon backbone. Under similar conditions, NR and SBR perform poorly.

Silicone rubbers used for coating textiles show excellent resistance to water (even at high temperature), but deteriorate at >130-140 °C. Their performance in acid and alkali media is very poor [14].

This elastomer matrix is inert and has very good resistance to physiological fluids. It is therefore suitable for use in various biological- and chemical-resistant applications.

Table 3.5 Moisture, alkali and acid resistance of different elastomers			
Polymers	Resistance to water	Resistance to alkalis	Resistance to acids
Natural rubber	V. Good	Fair	Good
Styrene butadiene	V. Good	Fair	Good
Polybutadiene	V. Good	Fair	Good
Polychloroprene	Good	Fair	Fair
Nitrile butadiene	Good	Excellent	Good
Butyl rubber	V. Good	Excellent	V. Good
E P D M	Excellent	Excellent	Good
Polysulfide rubber	Fair	Good	Poor
Silicone rubber	Excellent	Fair	Fair
Chlorosulfonated polyethylene (CSM)	Good	Excellent	Good
Polyacrylic rubber	Good	Poor	Poor

FA polysulfide rubber compounds have significant resistance to dilute acids and alkalis, but show poor performances against strong oxidising acids [21]. The properties of different elastomers with respect to resistance against moisture, alkalis, and acids are shown in **Table 3.5**.

### **3.2.8 Resistance to Oils and Solvents**

There are many applications for rubber-coated fabrics that are resistant to oil and solvents. Such applications include inflatable fuel-storage tanks, hoses, conveyor belts and flat belts, fabric-reinforced gaskets, diaphragms, aprons and footwear. For these applications textile fabrics are coated with an oil-resistant elastomer, and the coated textile utilised in the fabrication of items in an unvulcanised state. The green made-up articles are subsequently cured when the specific shape and design (especially if it is handmade) is completed. Vulcanised oil-resistant coated textiles are usually used for making aprons, linings, covers and tarpaulins for oil-refinery installations, and in food-processing industries where materials come into contact with animal/vegetable fats and oils [5].

Most conventional rubbers exhibit a high swelling tendency in aromatic and chlorinated hydrocarbons. The type of polymer and the percentage of rubber in the compounds are the main factors of oil resistance characteristics. In the environment of oils and solvents, the oil-resistant matrix of the rubberised fabric must not change into unusual dimensions or disintegrate during service.

The inherent properties of NR and SBR mean that they cannot be employed in oil-resistant applications that require long durations of use. However, ENR-50 can give oil resistance properties close to those seen for medium NBR, and is superior to that observed for CR. Its blending with EPDM can enhance ozone resistance.

Elastomer coatings based on the highly polar NBR provide excellent resistance to non-polar solvents such as fats and oils, mineral oils and petroleum hydrocarbons. This polymer with its high acrylonitrile content offers better resistance to oil in comparison to polymers with low proportions of acrylonitrile. The type of plasticiser used as the processing aid, amount of filler incorporated in the compound, and the system of crosslinking during cure affect the swelling tendency of the coating. The higher the crosslinking on vulcanisation, the better the resistance. The type of plasticiser in the compound is also important; the extractable type is to be avoided if the coating comes into contact with the oil for longer durations.

Table 3.6 Oil- and solvent-resistance of different elastomers										
Type of solvent	Natural rubber	Styrene butadiene rubber	Poly chloroprene rubber	Nitrile rubber	Butyl rubber	EPDM	CSM	Polysulfide	Polyacrylic	Silicone
Oils and greases	Poor	Poor	Moderate	Good	Poor	Poor	Good	Good	Moderate	Moderate
Animal and vegetable oils	Poor	Poor	Good	Excellent	Good	Good	Moderate	Excellent	Good	Good
Aliphatic hydrocarbons	Poor	Poor	Good	Excellent	Poor	Poor	Moderate	Excellent	Excellent	Moderate
Aromatic hydrocarbons	Poor	Poor	Poor	Good	Poor	Poor	Poor	Excellent	Moderate	Moderate
Halogenated hydrocarbons	Poor	Poor	Poor	Good	Poor	Poor	Poor	Good	Poor	Moderate
Oxygenated solvents	Good	Good	Poor	Poor	Good	Good	Good	Excellent	Poor	Good

CR-based coating compounds can be used in oil-resistant applications. They offer good resistance to naphthenic and paraffinic mineral oils, but swell in low molecular weight aromatic mineral oils. CSM (Hypalon 20 and Hypalon 30) provides good resistance to oil, but can be soluble in organic solvents.

EPDM elastomers have poor resistance to aliphatic and aromatic hydrocarbon oils. However, they exhibit good resistance to oxygenated organics, and to oils of animal and vegetable origin. Silicone rubber coatings are not resistant to chlorinated hydrocarbons, ketones or esters [12].

FA polysulfide rubber (Thiokol) has outstanding resistance to aliphatic and aromatic solvents, but is swollen by the aromatic solvent benzene. This elastomer is unaffected by alcohols, ketones and esters, and is also resistant to chlorinated solvents. It can also be blended with non-solvent-resistant elastomers to increase the solvent resistance for a particular group of solvents (e.g., blending with butyl rubber offers good solvent resistance to the blends). In leak-proofing applications, FA polysulfide-based putties are widely used to seal the joints of rubberised storage tanks for storing oils and solvents. The suitability of various rubbers in an atmosphere of oils and solvents is shown in **Table 3.6**.

A selection of different types of rubber for the compounding of coating fabrics exposed to various solvents is shown in **Table 3.7**.

<b>Table 3.7 Selection of elastomers in different solvents</b>	
<b>Solvent</b>	<b>Elastomers</b>
Aliphatic hydrocarbons	CR, NBR, CSM, polysulfide rubbers, polyurethane rubbers
Aromatic hydrocarbons	Fluorosilicone rubbers, fluorocarbon rubbers
Chlorohydrocarbons	Fluorocarbon rubbers
Alcohols	Natural rubber, SBR, EPDM, IIR, CR, CSM, polysulfide rubbers
Ethers	polysulfide rubbers, fluorocarbon rubbers, polyurethane rubbers
Ketons	EPDM, IIR, polysulfide rubbers
Esters	EPDM, IIR, polysulfide rubbers



### **3.2.9 Flame Resistance**

The pursuit of a wide variety of domestic, civil engineering, industrial and military applications of rubber-coated fabrics means that the latter may be required to be flame-retardant, flame-proof, or to be able to reduce the risk of fire hazards. Some of the rubbers burn easily if they come into contact with an open flame because most of the rubber molecules are composed of hydrogen and carbon. Correct selection of the polymer for these applications is extremely important.

CRs are inherently flame-resistant because of the chlorine content in the molecules. In this respect, CRs are superior elastomers to most other rubbers. Compounded and cured CR may decompose upon contact with flames, decomposition will not continue when the flame is removed. Liberation of chlorine from the elastomer helps to extinguish the flame. The mix should not contain any flammable ingredient (e.g., mineral oils) which may be used as a processing aid in the formulation.

The flame resistance of this rubber may be further enhanced by incorporation of phosphoric acid ester as a plasticiser, chlorinated hydrocarbons, and antimony trioxide in the compounding formulation.

To reduce the fire hazard of the CR-based rubber compounds used for coating fabrics, inclusion of antimony trioxide at a higher proportion, and zinc borate to form a crust helps to resist propagation of the flame.

Simultaneously, chlorine is liberated from the halogen-containing rubber and associates with antimony trioxide to form antimony trichloride, which suppresses propagation of the flame and ultimately extinguishes it. The use of phosphate-based plasticisers in the mix may be necessary to improve the result.

Chlorinated paraffinic hydrocarbons (viscous yellowish liquids) with ~72% of chlorine content are used as the active fire-retardant ingredients in NR, SBR, CR and other diene rubbers.

The cure may retard slightly if the compound contains sulfur and accelerators as curatives but, with a metallic oxide curing system such as CR rubber mixes, this can accelerate the cure. They can be safely used in textile coating compounds that come into contact with the human skin without irritating effects because they contain chlorine.

In flame-resistant coating stocks based on non-halogen-containing elastomers, a combination of chlorinated paraffins, antimony trioxide (20 phr), zinc borate (4 phr), magnesium carbonate and aluminium oxyhydrate/trihydrate is useful to obtain satisfactory results.

Chlorinated NR is available in powder form. It may be included in the formulation for fabric coating (particularly if processed in solution spreading as a flame-proofing ingredient). This can be an ingredient for a compound of lower flammability, and improve the adhesion of the coating mixes.

For synthetic rubbers which do not contain chlorine in the molecule, phosphate plasticisers are generally used to improve the flame retardancy. In halogen-free compounds, hydrated alumina as filler can give good flame-resistance [7].

Other than CR, halogen-containing rubbers such as chlorosulfonated polyethylene (Hypalon) and fluorocarbon rubbers show good flame-resistance because of their inherent flame-retardant property.

In reducing the combustibility of the coated rubber matrix, compounds based on NR and synthetic rubber, incorporation of hydrated alumina as filler, and highly chlorinated paraffin (chlorine content = 72%) can provide the desired result. Also, combination with antimony trioxide enhances the flame resistance in halogen-free compounds.

The use of zinc borate with chlorinated paraffin helps in the formation of a intumescent hard crust which restricts flame propagation when the product comes into contact with an open flame. Protection from the flame can be increased by using phosphate plasticisers such as chloroalkyl phosphate [2].

Processing ingredients such as factices, mineral oils, and waxes aid flammability, so a minimum amount should be used in flame-resistant compounds for textile coating.

In high oil resistance applications where the use of nitrile rubber is necessary, improved flame retardancy can be achieved by selecting nitrile/PVC blend elastomers. To further improve this property, tricresyl phosphate as a plasticiser may be included in the formulation. The flame suppressants discussed previously are also useful in obtaining better efficiency.

Formulations based on polyacrylic elastomers can be made flame-resistant by incorporation of hydrated alumina, antimony trioxide, chlorinated hydrocarbon, and phosphate type plasticisers [20].

The test of flammability of a sample is called the limited oxygen index (LOI) according to the procedure given in standard ASTM D2863. It indicates the percentage of oxygen support in combustion. A material having an LOI of >30 is considered to be flame-retardant and a material is considered flame-proof at >50 [21]. The LOI of different rubbers is shown in **Figure 3.2**.

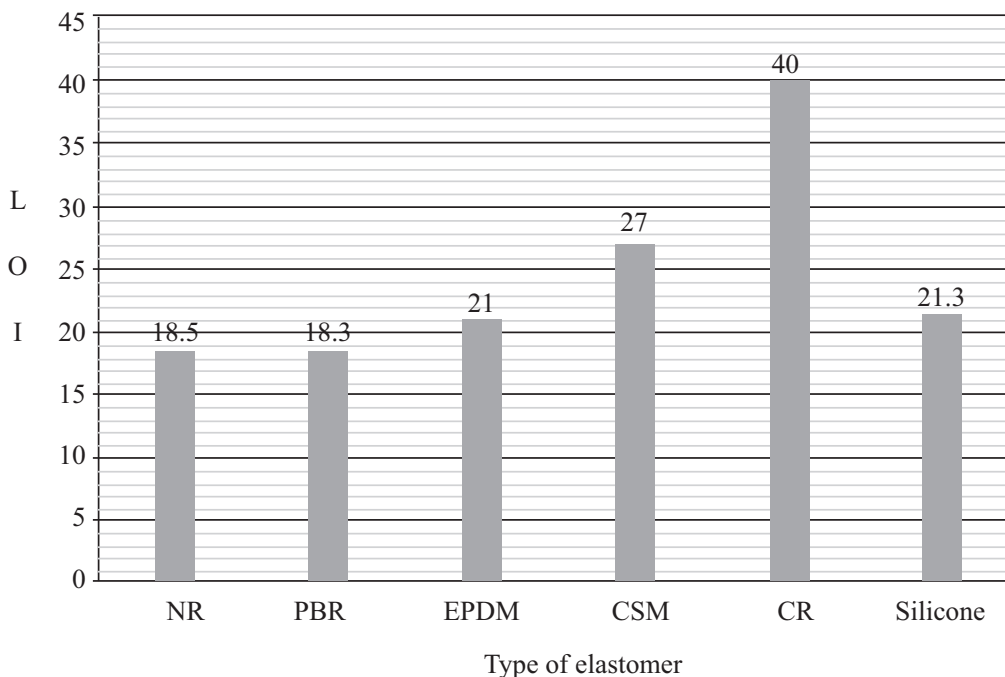


Figure 3.2 Values of the limited oxygen index of rubbers

### 3.2.10 Rot-proofing, and Resistance to Attack by Fungi and Insects

Rubber-coated fabrics are prone to fungal attack, particularly if exposed to a humid and wet atmosphere which speeds up the rotting of the material. This phenomenon is a common problem when NR-based coating compounds are applied on natural fibre. To provide the rot-proof property, anti-fungal treatment may be necessary on the basic textile. Additives can be added to the rubber mixes to protect the coated product from fungal attack.

Special-purpose synthetic rubbers are not usually prone to this problem in comparison with NR and general-purpose synthetic rubbers.

Incorporation of bactericides and anti-mycotic agents and some of the active ingredients into the mixes help to overcome the deteriorating effect of rubber-coated fabrics.

In some tropical and sub-tropical countries, the rubberised fabric may be infested with 'termites'. These can also destroy the material if used outdoors or if the fabric comes into contact with soil.

The use of anti-microbial chemicals in the coating compounds helps to prevent the coated fabric from attack by micro-organisms, fungi and other microbes. A mixture of phenols and sulfur compounds (Antimykotikum A, Bayer) and another compound based on dihydroxy-dichlorodiphenylmethane (Preventol GD, Bayer) are available in powder form and can be incorporated in the proofing compound at 4 phr to obtain excellent results. Antimykotikum A can be used at 1-3 phr to obtain satisfactory results [6]. These protective chemicals do not affect the processing behaviour of the mixes. They enable the coated fabric product to destroy bacteria, fungi, or pathogenic yeasts or to inhibit their development.

Excellent results can be achieved for very long-duration uses by impregnating the fabric (usually a natural fibre with Preventol GD in solution form after dissolving the chemical in solvent) and adding Antimykotikum A directly to the mix used for friction coating (as an anchor coating for subsequent coating) in a calender machine.

Antimicrobial prevention can be further enhanced through the addition of rubber accelerators such as zinc dithiocarbamate or thiuram accelerators. Protection against fungi, bacteria and other microbial action can be obtained by using Antimykotikum A alone in the compound. This chemical can quickly destroy many micro-organisms and vastly inhibit their development.

Incorporation of some suitable acidic antimicrobial agents in the rubber coating compounds, such as salicylaldehyde and dihydroxy-dichlorodiphenyl methane derivatives, provides very good protection. Zinc dithiocarbamates and thiurams can be considered to offer mild resistance.

The best results can be obtained by using furylbenzimidazole, but its use is restricted because it is allergenic. The carboxylic acid group of benzenecarboxylic acid (benzoic acid) can inhibit the growth of micro-organisms such as yeasts and other unicellular fungi that are sometimes visible on the surface of unprotected rubber coatings [8].

A chemical composition that is termite-repellent, a phosphoric acid ester (Termite Repellent K, Bayer) or a mixture of chlorinated phenols can be added to the rubber mixes as insecticides. These are non-hazardous to the processors and the user. These chemicals can be safely used at 3 phr in the elastomer mixes based on NR, SBR, CR, NBR, butyl rubber and silicone rubber compounds implemented for coating textiles. They can provide resistance to termite infestation to the coated products for several years [22].

### **3.2.11 Odorants and Flavouring Agents**

The typical rubber odour and the unpleasant smell of rubber chemicals which may be enhanced after vulcanisation of the rubberised fabric may be undesirable for certain uses. This intrinsic odour of NR and synthetic rubber can be minimised during long storage under ventilation or can be treated with steam. The odour cannot be completely removed.

Addition of odour improving ingredients to the rubber compound during mixing can transform the odour. It can also be completely disguised by the sweet smelling perfume of flowers or fruit. The odour of leather for leather substitute-coated textiles or a fresh laundry odour can be incorporated in coating mixes for domestic uses of rubberised fabrics.

In some rubber coating compounds, adding pine oil in combination with vanilla (methoxybenzaldehyde) disguises the rubber odour and can impart a pleasant smell to the product. It may be necessary to construct the rubberised fabric with a desirable smell if the fabric is used for hospital bedspreads, waterproof garments or aprons.

Pleasant-smelling odorants of various aromas are available (e.g., Rubberol-F, Bayer). This liquid ingredient can be compatible with the rubber mixes if based on NR and synthetic rubbers. The usual amount used to disguise the intrinsic smell of rubber is 0.1-0.2 phr, and for perfuming purposes is 0.5-1 phr. It can give a long-lasting fragrance to the coated product.

To neutralise the characteristic rubber odour, Rodo Number 0 (Vanderbilt) and to impart a pleasant floral scent Rodo Number 10 (Vanderbilt), as blends of essential oils, may also be considered in the coating mixes. The usual amount may be 0.2-0.5 phr, which is sufficient for the long-duration fragrance of the product [6].

Many basic perfuming agents and floral fragrances are available for masking unpleasant odours. They can also be incorporated into the mixes to impede the characteristic odour of rubber and that of other ingredients. However, their compatibility with rubber compounds of different elastomers must be carefully studied before use.

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# 4 Natural and Synthetic Textiles Used in Polymer Coatings

**Bireswar Banerjee**

## 4.1 Introduction

A rubber-coated textile composite is produced to improve mechanical properties, impart adequate strength, and to maintain dimensional stability, durability, impact strength and toughness.

Textiles used as fundamental reinforcing agents for elastomer-coated items are categorised into three groups:

- Fibres of natural origin (available from plants and animals).
- Synthetic polymers of chemical origin.
- Inorganic or metallic fibres (e.g., glass, steel, and asbestos) of mineral origin.

Among those considered for use as reinforcing materials to produce a rubber fibre composite, cotton, Rayon, polyamide, polyester, glass and steel fibres are the most common. Fibres obtained from animals are usually not coated with dry rubber compounds. However, latex backing for carpets in which animal wool is used is a common product in the latex-coating industry [1].

Cotton fibres are widely consumed as woven fabrics for rubber coating in general use, and produce soft and absorbent textiles. Jute fibres are hard and brittle plant fibres which can be used for rubber coating. Man-made fibres are mostly produced from wood pulp, cotton linters, or petrochemicals. These chemicals are generated from crude oil and natural gas. The fibres manufactured from petrochemicals are polyamide, polyester, acrylic, and olefinic fibres. In general technical applications, excellent strength can be acquired from polyamide.

The term 'technical textiles' is customarily applicable for textile materials. The polymeric coatings in the end-product are dependent upon the technical performance and functional properties required.



To limit the use of cotton textiles (which are natural fibres), and to increase the durability and performances for rubber-coated material, research and development into synthetics started in 1900. Viscose Rayon was the first fibre to be described as a 'man-made' fibre. It was introduced for making tyres in the 1920s.

This fibre was initially marketed as 'artificial silk' because its lustre resembled that of natural silk threads. The term 'Rayon' was adopted in 1924. High-tenacity Rayon was developed in the 1940s.

Synthetic yarns were developed when Nylon fibre was marketed by DuPont in 1938. Polyester fibres were produced in the UK in 1951 and introduced in the USA in 1953 by DuPont. Nylon is a polyamide fibre, and a variant aromatic polyamide fibre called Kevlar was introduced by DuPont in 1973. This aramid fibre was used as a reinforcing material for polymer composites in the 1980s, and is still used in several areas.

Glass textile fibre is an inorganic substance manufactured from glass and was introduced in the 1920s. Fibreglass was produced in 1938 to be used as insulation. Some of its properties (e.g., flame-proof behaviour, heat resistance, non-absorbency, resistance to sunlight and most chemicals) find use in specific industrial purposes upon coating with elastomers. During the late 1960s, it was used for making tyres in the USA. Its uses as an reinforcing material are evolving; glass cord has been introduced in the manufacture of rubber driving belts.

Another inorganic material with extraordinary properties, steel cord, was introduced in 1963 for making tyres. The use of steel cords in the reinforcement of rubber items started in the 1970s. Michelin included steel tyre cord in the manufacture of tyres in 1971 to improve performances. The steel has continuing use as a remarkably good reinforcing material, specifically in making tyres and rubber conveyor belts. High-tensile fine steel wire reinforcement in rubber hoses is widely used in high-pressure applications [2].

In the process of weaving the fabrics, weft insertion using a conventional shuttle system, increasing the speed of insertion of weft thread, and the development of rapiers, air jets, and water jets have increased the output. Using high-speed knitting machines, the making of non-woven fabrics has been introduced in the textile rubber-coating process to meet the explicit requirements of the coated material. Rubberised textiles and cords as well as metal cords have been used to reinforce tyres, belts and hoses. Elastomer-coated textiles, cords, metal cords and meshes are in use in various industrial applications.

## **4.2 General Criteria for the Selection of Textile for Polymer Coatings**

Woven, non-woven, corded, knitted, and braided materials are utilised for coating with rubber to impart dimensional stability, strength, load-carrying capacity, as well as to provide resistance to impact and pressure to the final rubber product. Non-woven fabric, if coated with absorbent material mixed with compounded elastomers, provides gas-absorbent properties for certain military applications.

The basic requirements to be taken into consideration with respect to the specific end-use of a coated fabric are:

- Type of fibre
- Construction of the selected fabric
- Mechanical properties

These important requirements may be the ‘guidelines’ for a textile manufacturer to produce and supply the preferred material for coating [3]

### **4.2.1 Choice of Textiles for Rubber Coating**

The selected textiles used for coating should have the following characteristics:

- Facilitate processing.
- Appropriate adhesion with the rubber matrix.
- Provide dimensional stability to the final product.
- Contribute high breaking strength to the product.
- Adequate resistance to tear.
- Flexible and resilient.
- Provide resistance to periodic bending fatigue.
- Confer resistance to elevated temperature.
- Have low shrinkage on heat.
- Resistance to abrasion.

- Low moisture regain.
- Be rot-proof.

Mechanical properties such as breaking strength and tear strength are the principal criteria for the selection of the textile for the industrial use of the coated fabric. Adequate fatigue resistance of the product under high stress and strain is also important.

Adhesion of the fabric with the rubber matrix is dependent upon the nature of the fabric as well as constructional factors. The important criterion of ensuring bondability to fabrics with rubber is to prevent the rubber coating separating out during service on high-flex zones or if functional in high-tension areas.

Because of the staple fibre ends of cotton, mechanical anchoring with the rubber layer is possible. The pressure provided to penetrate the rubber into the interstices of the fabric by a spreading machine or by the rolls during calendering helps in adhesion to the rubber matrix. However, in man-made fabrics, the continuous filament structure requires chemical treatment to improve adhesion with the rubber cover.

The dimensional stability of the coated fabric, the change in shape due to shrinkage during vulcanisation, and excessive elongation of the inflated products during the service life must be controlled with respect to the elongation property and construction of the basic fabric. Synthetic fabric may need to be heat set to the extent of the elongation limit to control this problem [3].

High moisture regain affects adhesion to the fabric due to a moisture layer on the surface of the fibres and also invites attack by mildew, particularly when the product is used in a humid atmosphere.

Adequate heat resistance is necessary for the coated fabric if it is used in making heat-resistant products. Cotton shows better heat resistance in comparison with man-made/synthetic fabrics because some synthetic fabrics have a low softening point if the temperature is increased.

The fabric on the rubber matrix should impart the desired elongation and flex properties in relation to the extensionability of the rubber to prevent the rubber layer separating out of the substrate.

The fabric, irrespective of whether it is processed for coating on a rubber calender machine or in a spreading machine, must be appropriately designed to withstand distortion due to the roll pressure and tension during coating. The surfaces of the

textile must be designed appropriately to facilitate coating with highly viscous elastomers [3].

For the fabric to be rot-proof, anti-fungal treatment on the basic textile may be necessary. Additives can be added to the rubber compounds to prevent the coated products from fungal attack [4].

To improve the flame resistance of the coated material, selection of the textile and the addition of special ingredients to the rubber mix are important. The technical parameters of different fibres and their adhesion properties with rubber are listed in Table 4.1.

Table 4.1 Comparative properties of different fibres for rubber coating							
Type of fibre	Density g /cc	Tenacity (grams/denier)	Flexibility	Heat-resistance	Rot proofness	Bondability	Treatment necessary to improve adhesion
Cotton	1.52	4. 0	Good	Good	Poor	Very good	Not necessary
Rayon	1. 48	2. 5	Good	Poor	Moderate	Poor	Necessary
Nylon	1. 14	7. 2	Very good	Poor	Very good	Poor	Necessary
Polyester	1. 40	7. 0	Very good	Poor	Very good	Poor	Necessary
Aramid (Kevlar)	1. 45	5. 3	Low	Excellent	Excellent	Poor	Necessary
Silk	1. 33	4. 5	Very good	Good	Moderate	Poor	Necessary
Glass	2. 56	9. 6	Low	Excellent	Excellent	Poor	Necessary
Carbon Fibre	1. 95	15. 9	Good	Excellent	Excellent	Good	Necessary
Steel	7. 8	4.0	Poor	Excellent	Poor	Poor	Necessary

## 4.3 Reinforcing Fibres and their Origins for Application in Elastomer Coatings

### 4.3.1 Natural Origin Fibres

Natural origin fibres such as vegetable fibres and cotton are composed of 100%

cellulose, with short staple lengths of 10-20 mm. They offer high bulk and low strength, but are susceptible to microbiological attack.

#### **4.3.2 Man-made Rayon Fibres**

Man-made Rayon fibres are rejuvenated cellulose, they can be continuous filament yarns and produced in a staple form. Rayon has a higher tenacity than cotton and its moisture regain is high. Heat setting is required before coating to control shrinkage.

#### **4.3.3 Fibres of Organic (Man-made) Synthetic Polymers**

##### **4.3.3.1 Nylon**

The common example is polyamide (Nylon). Nylons are usually continuous filaments with high tenacity and low moduli. Nylons have excellent resistance to abrasion and fatigue, with good impact resistances. Heat setting is required before coating to control shrinkage during vulcanisation upon rubber coating.

Synthetic fibres demonstrate high strengths which makes them suitable for specific technical uses with rubber-coated products. However, this property can be further enhanced if more strength is required by aligning the orientation of the molecules through strengthening intermolecular forces by stretching. Fibre molecules move freely to relieve stress within the fibre at a certain temperature and the fabric is kept under tension up to the time of cooling to maintain the shape of the molecular structure of the fibre. By combining drawing with modification of the length of the molecular chain, high-tenacity fibres can be produced.

##### **4.3.3.2 Polyester**

Polyesters can give rise to organic, continuous filament yarns whose tenacity is higher than that of Rayon and Nylon, and which have a much higher modulus, lower extensionability, and low moisture regain.

The organic polymer fibres of polyesters are highly anisotropic (i.e., possessing different physical properties in different directions). Hence, heat stretching is usually necessary to arrange the chain molecules parallel to the axis of the fibre. In this way, a stronger material with higher melting temperatures can be obtained.

#### **4.3.3.3 Aramid**

Aramid is an organic polymer (aromatic polyamide) with a continuous filament yarn. It has the highest tenacity of all polyesters and the lowest elongation at break. Aramid is a polymerisation product of an aromatic diamine and terephthalic acid. High-modulus and pretreated aramid yarns are produced for their improved bonding to rubber.

#### **4.3.4 Non-Polymeric (and Man-made) Fibres**

##### **4.3.4.1 Steel Fibre**

Steel fibre is composed of 0.70-0.85% high carbon steel. It is drawn to the required filament diameter of 0.15-0.40 mm in the form of cable to make cords. Final drawing of the wire creates a fibrous metallic texture.

Steel cords have high tensile strengths and very low extensibilities during service. However, they have good flexibility and good fatigue resistance.

A zinc/brass coating must be applied on the steel cords to implement good bondabilities to the rubber and to prevent corrosion. During brass plating, the wire is cleaned by acid pickling and subsequently rinsed with alkali/water to prepare the steel for the application of the brass coating at 4-8 g/kg.

##### **4.3.4.2 Fibres of Mineral Origin: Asbestos**

Asbestos is a fibrous amphibole. Amphibole is the name of an important group of rock-forming metasilicates (fibrous silicate minerals). These naturally occurring siliceous fibres are composed predominantly of calcium and magnesium silicate. Asbestos can be used as a heat insulating material and to fire proof coated fabrics. This mineral fibre can be spun and woven, and made into fire proof elastomeric-coated textiles for use as flame-resistant clothing. If coated with appropriate rubber compositions, asbestos fibres exhibit resistance to heat, chemicals and electricity.

#### **4.3.5 Synthetic (Man-made) Polymers of Inorganic Origin**

Fibre glass is a manufactured continuous filament fibre of inorganic origin. The

chemical composition of glass fibres is aluminium, boron oxides, calcium, silicone dioxide and small percentages of sodium and magnesium oxides.

Assembled strands of fibre glass are processable into yarn and can be woven using conventional textile machinery. This fibre is brittle with poor flex resistance, has low elongation, and excellent elasticities in a narrow range. Glass fibres are flame proofed to give high resistance against heat and chemicals, and exhibit good insulation properties.

Melted glass can be drawn into thin fibres with diameters of 0.005-0.01 mm. They can also be spun into threads and woven into fabrics. Glass fibres and fabrics become strong and flexible if coated with rubber.

Glass and metal fibres are isotropic (i.e., show uniform properties in all directions). Hence, to get optimal properties, the fibres do not require additional stretching [5].

The textiles used in reinforcing elastomeric products are:

- Woven
- Knitted
- Corded
- Braided

#### **4.3.6 Cotton**

The short staple cotton fibre is of natural vegetative origin. It is composed of 100% cellulose, containing carbon, hydrogen, and oxygen atoms and hydroxyl (-OH) groups. The basic monomer of cellulose is glucose. There may be as many as 10,000 glucose monomers per molecule connected in long linear chains and arranged in a spiral form within the fibre. The chemical reactivity of cellulose is related to the hydroxyl groups of the glucose unit. These groups react readily with moisture, dyes, and finishes. This type of treatment may be necessary if the elastomer-coated cotton fabric is converted in fabricating protective garments and domestic-use articles. The properties of cotton fabric are given in **Table 4.1**.

The cotton plant is a shrub that grows in tropical and subtropical regions. The soft fibres that grow around the seeds of the cotton plant offer high bulk with moderate strength. In elastomeric-coating applications where the requirement is considerable bulk and not very high strength, cotton textiles are the correct choice. The staple

length of cotton ranges from 10 mm to 20 mm, and contributes greatly to adhesion promotion by mechanical anchorage between the rubber matrix and substrate.

The ‘mercerisation’ of cotton involves treating cotton fabrics with sodium hydroxide. This causes a permanent physical change and increases absorbency, lustre, and strength. This treatment may be necessary if the coated material is transformed while making garments such as rain jackets and other personal protective items [6].

Cotton fibres may be blended with synthetic fibres for providing adequate strength and to promote adhesion properties. Blending of cotton with other fabrics is done to improve its buoyancy and elasticity.

The stress–strain properties of cotton (along with a comparison with other fibres) are shown in **Figure 4.7**.

Long staple cotton produces stronger yarns because there are more contact points among the fibres if they are twisted together. Cotton fibre having a dry breaking tenacity of 3.5–4.0 g/d (grammes per denier) shows a medium-strength range; wet cotton fibre becomes 30% stronger, it gives low elasticity, and the elongation is ~3%. The abrasion resistance of cotton is good. Higher weight fabrics are more abrasion-resistant than thinner fabrics. Heavy canvases are used to reinforce conveyor belts and hoses on coating with rubber to obtain more resistance to abrasion in addition to greater strength.

#### ***4.3.6.1 Processing of Cotton Fabric***

(i) **Ginning** is the process of separating cotton fibres from the seedpods (usually done in the cotton field using machines).

(ii) **Spinning** follows on from ginning. It is the making of yarn from cotton fibre. Different thickness of yarns are produced at this stage.

(iii) **Weaving** is the most important process in the making of textiles. Two or more yarns are placed to make the warp and weft of a loom, which consecutively turns them into a woven cloth.

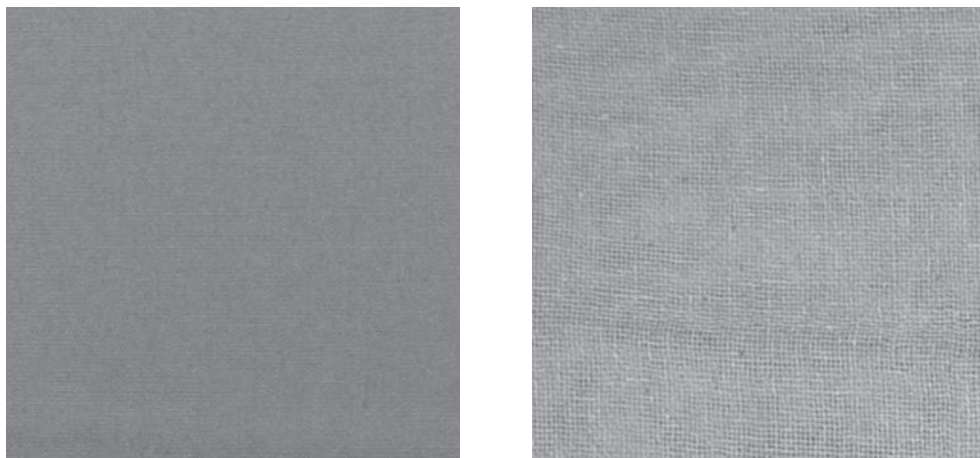
#### ***4.3.6.2 Finishes and Treatments of Cotton Fabric***

After weaving, the cotton fabric passes through different processing stages until it becomes the final product:



- Desizing involves removing the sized material from the warp yarns in woven fabrics.
- Scouring is the cleaning of fabrics with the help of textile processing scouring equipment to remove soil, chemicals, waxes and oils that may be used in making the fabric.
- Bleaching the woven fabric makes it whiter and lighter. It removes stains and prevents yellowing of the fabric.
- Mercerising involves immersing the fabric in alkali solutions to make the textile stronger, more shiny, more durable, and free from unusual shrinkage.
- Dyeing is a colour treatment with the specific shade of dye according to the requirement of the coated end product.
- Finishing – during this process, fabric is treated with certain chemicals to make it better qualitatively. That is, sometimes cotton fabric is treated with ultraviolet (UV) protecting agents such as optical brighteners, dyes and chemicals. This requirement is particularly important for one-side-coated textiles because the uncoated surface of the fabric will remain exposed [6].

Plain-weave cotton fabric swatches are shown in **Figure 4.1**.



**Figure 4.1** Plain-weave cotton fabrics

#### **4.3.6.3 Characteristics of Cotton Fabric**

- Cotton fabric imparts good strength. It is soft and comfortable but wrinkles easily.
- It has excellent absorbing capabilities.
- Cotton is moderately flame-retardant.
- Blending of cotton gives buoyancy and elasticity.
- Adhesion with rubber is very good even without chemical treatment.
- Processability with rubber coatings is good.

#### **4.4 Jute Textile Fabric**

Jute is one of the cheapest textile fibres. It is composed of ~60% cellulose. It is obtained from the jute plant grown throughout Asia. The primary fibres in the fibre bundle are short and brittle, and extension at break is low, making jute one of the weakest of the cellulosic fibres. With the help of processing machines, jute fibre can be made thinner and smoother, so that it can be used for rubber coating. When blended for the reinforcement of polyester fibre, high-modulus jute can partially substitute for glass fibre [5].

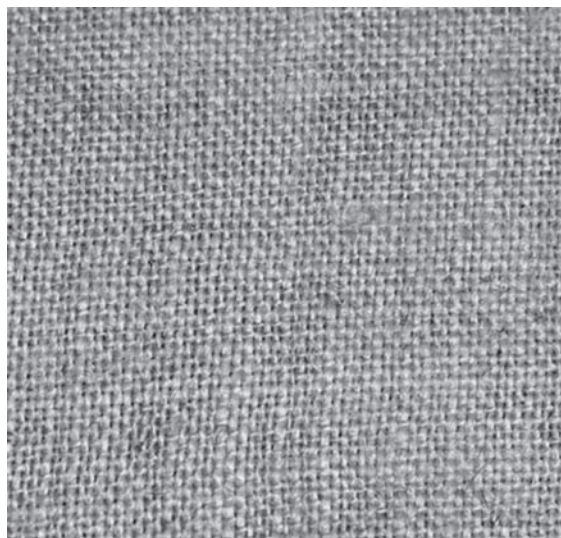
The most suitable climate for cultivation of jute is offered by the monsoon climate. A temperature ranging from 20 °C to 40 °C and relative humidity of 70-80% are favourable for growing jute. Jute is graded according to its colour, strength, and fibre length. The fibres are off-white to brown in colour, and available 1-4 metres long. The fibre is soft, lustrous, and pliable when first removed from the stalk.

Woven jute is strong and durable, eco-friendly, versatile and economical. Jute yarns can be spun on a standard carding system, drawing, and spinning frames. This fibre can be vat- and acid-dyed to produce fast colours. Jute, if used as a reinforcing fibre coated with polymers, can be utilised in low-cost housing, tents, and in geotextiles.

This fabric is widely used in packaging. With durable natural elastomeric coatings, its performance may be improved substantially for packaging and eco-friendly cheap carrier bags. Woven jute fabric is shown in **Figure 4.2**.

Jute fabric is commonly called 'hessian'. It is a plain weave cloth made entirely of jute with single warp and weft interwoven weighing  $\leq 576 \text{ g/m}^2$  [6]. This hessian can be implemented for rubber coatings. Lighter-weight hessian can be blended with cotton or synthetic fibres to increase strength and improve surface finishes. It may be coated

with elastomer to make it suitable for waterproofing and geotextile applications. Use of an appropriate elastomeric coating can make the jute fibre more durable, and can protect against deterioration if used as a geotextile. Elastomer-coated jute fabrics can be used for making shopping bags, soft luggage, floor coverings, and erosion-control applications. Non-woven jute felt that ranges from 250 g/m<sup>2</sup> to 1200 g/m<sup>2</sup> can be used for industrial insulation, acoustics, insole liners of footwear, and upholstery backing on suitable rubber coatings by solution spreading or spraying. Elastomeric-coated jute fabric is strong; provides good insulation to heat and electricity; is environmentally friendly if coated with biodegradable natural rubber; and is repairable and reusable when used in civil construction. Jute fibre emits fumes which do not have an adverse effect on the human body. The moisture regain of jute is high (~12.5% at 65% relative humidity). This criterion should be taken into consideration before coating.



**Figure 4.2** Jute textile for rubber coating

Rubber-coated jute can be used as technical textiles and composites. Hence, elastomer-coated jute textiles have other possible uses. This natural fibre, if lightly woven and coated with rubber, can be used for control of soil erosion and landscaping uses. Biodegradable coated jute geotextiles that are left to rot on the ground help to keep the ground cool and make the land fertile [7].

#### **4.4.1 Characteristics of Jute Fabric**

- Moderately high density; high modulus.
- Strong, good insulator of heat and electricity.
- Stable to sunlight but change of colour may occur if exposed to sunlight.
- Fibre is not sensitive to moderate attack by chemicals.
- Photochemical degradation may occur on exposure to UV light.
- Jute fibre is environmentally friendly and economical.

#### **4.5 Rayon**

Rayon is produced from naturally occurring polymer (mostly from wood pulp). It can be made from regenerating natural materials into a usable form. It is economical, and can be used in cotton-like end-uses for elastomer coatings. This fibre is usually obtained as continuous filament yarn, but can also be produced in a staple form (from rejuvenated cellulose). To produce a staple fibre, specific chemical processing is necessary. Staple fibres and tow (a large assembly of filament fibres to facilitate processing during the production of staple fibres) range from 1.5 denier to 15 denier.

Rayon filament yarns range from 80 filaments per yarn to 980 filaments per yarn, and vary in size from 40 denier to 5000 denier. A mechanical/chemical process is used to crimp staple fibres.

The process of producing Rayon filaments or staple fibres begins with dissolving processed cellulose in caustic soda. The solution is then pressed to remove excess liquid, and exposed to oxygen. It is then dissolved in caustic soda to form viscose. Viscose solution is extruded through a spinneret and lands in a bath of sulfuric acid to form Rayon filaments. It is then stretched and washed to remove residual chemicals. Rayon can also be made in a staple spun form to provide bulk if the provision of high strength is not important.

A modified version of viscose has greater strength when wet. It is known as ‘high wet modulus (HWM) Rayon’ and can also be mercerised like cotton. Another modified version of viscose that is double the strength of HWM is ‘high-tenacity Rayon’. This is typically industrial Rayon used in making rubberised tyre-reinforcing cords [8].

The wet spinning method is the most common process for producing Rayon. Purified cellulose is chemically converted to a viscous solution, forced through spinnerets into

a batch, and returned to 100% cellulose filaments. It maximises chain length and fibril structure if the HWM process is followed. In HWM Rayon, ageing is eliminated and the molecular chains are not shortened.

This manufactured fibre composed of regenerated cellulose and substituents have replaced  $\leq 15\%$  of the hydrogens of the hydroxyl groups. To distinguish it from viscose Rayon, it is referred to as 'HWM'. This grade of Rayon fabric has stability and strength equal to that of cotton [6].

HWM gives high wet strength, and can be mercerised for increased strength. Rayon is produced from regenerated cellulose, so it is biodegradable. The properties of Rayon fabric are similar to those of natural cellulose fibres such as cotton.

Modified Rayon shows exceptional strength. It is used primarily for making tyre cord upon rubberisation. Rubberised Rayon fabric can be used for making protective garments (e.g., rainwear, snow jackets). It can be dyed to give colour; maintains dimensional stability and strength during use; is durable, highly absorbent and resistant to abrasion; and has good breathability.

Rayon has low resilience, elastic recovery, and dimensional stability. These properties can be improved in HWM Rayon fabrics by adding a wrinkle-resistant finish. However, the finish may decrease the strength and abrasion-resistance of Rayon. Compared with cotton, the tenacity of Rayon is higher due to its high moisture regain. Adhesion with the rubber matrix during coating and vulcanisation may adversely affect moisture absorption.

The fibre becomes very weak when wet. If Rayon is used as reinforcement, there may be a loss of strength when moisture is absorbed through the exposed ends of the fibres, and this may reduce the strength of the fabric, however, HWM Rayon performs better than this.

Hence, it is essential to cover the Rayon fabric ends with the elastomeric coating to prevent water ingress. To improve adhesion with the rubber matrix, dipping of Rayon textiles in resorcinol formaldehyde latex adhesive is necessary [7].

#### **4.5.1 Characteristics of Rayon Fabric**

- Strong, durable, breathable, absorbent, but not free from wrinkles.
- Good resistance to abrasion.
- Can be readily dyed to give colour.

- Can resist damage by insects.
- If wet, it loses strength by 30-50%.

## **4.6 Nylon Textiles**

The excellent properties of this fibre (lightweight, high-strength, resistance to abrasion, very good elasticity, resistance to chemicals, and heat-setting) make it suitable for many technical applications if it is coated with elastomers. The comparative properties of Nylon fibre are given in **Table 4.1**.

Various substances are used to make polyamide. The elements contained in the recurring amide groups are carbon, oxygen, nitrogen and hydrogen. It has long molecular chains which are straight and variable in length without any side chains. A number is put after the word Nylon to indicate the number of carbon atoms in the starting materials (e.g., Nylon 6 or Nylon 6,6).

The Nylon 6,6 grade is widely used as technical fibre. It is made from hexamethylene diamine and adipic acid, both of which have six carbon atoms. The acid-to-base ratio of 1:1 forms a salt or Nylon salt. The salt is heated under vacuum. After drying to eliminate water, the polymer is formed. Production of Nylon 6 starts with pure caprolactam as a single substance having six carbon atoms and uses a ring-opening polymerisation. Caprolactam is heated in an inert atmosphere of nitrogen for 4-5 hours; the ring breaks and undergoes polymerisation. The molten mass is then passed through spinnerets and solidifies to form fibres of Nylon 6,6 [9].

In the process of manufacturing synthetic fibres, the filament yarns are prepared by extruding the polymer solution through a spinneret followed by solidifying the solution as it emerges from the spinneret. Filaments are brought together collectively with twisting or without twisting; they are then grouped together and twisted again to make filament yarns. In a spinning machine, the yarns are wound on a bobbin. The yarn is rewound on cones or spools and taken as the finished product. In some cases, treatment such as crimping, twisting, texturing or finishing may be necessary. A close-up view of a Nylon fabric swatch is shown in **Figure 4.3**.

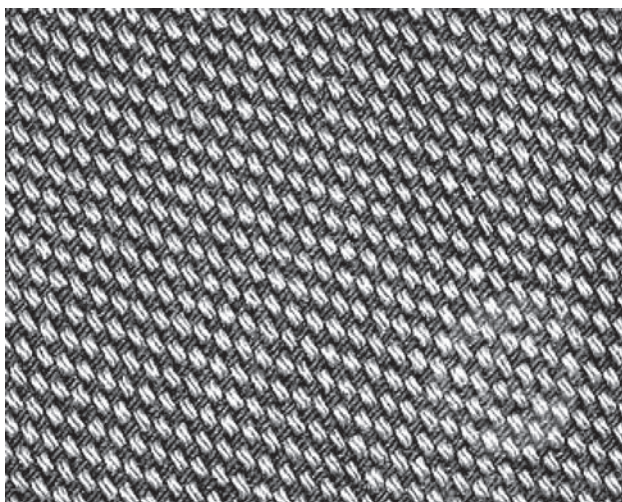
During the processing of continuous filaments, a size is applied at 0.5-2% by weight after the fibre is drawn; it protects the fibre during winding on the bobbin. The type of size is selected based on the end-use of the fibre. This may be a processing aid (particularly if the fibres are used in a composite). Specific sizes are applied which make the fibre resemble a certain resin.



Nylon is available in a wide range of deniers in multifilaments, monofilament, and in a staple form of various lengths. The filament is uniform and has a round cross-section. The fibre looks like fine glass rods if observed under light microscopy. Nylon can be solution-dyed to obtain the desired colour shade, but dyeing of Nylon 6,6 is difficult.

Nylon 6 can be heat-set at 150 °C and its softening point is ~220 °C. Nylon 6,6 can be heat-set at 205 °C, and its softening point is 250 °C. Nylon 6 has good elastic recovery and fatigue resistance, and shows better resistance to the weather and sunlight than Nylon 6,6.

Nylon has very good abrasion resistance, excellent tenacity, high elongation, good resilience and high dimensional stability with low moisture absorbency. With these exceptional properties, Nylon can be used in several technical and industrial uses upon coating with suitable elastomeric compounds. It also has excellent resistance to alkalis, but dissolves in formic acid and phenol. In general, Nylon is resistant to insect attack, rot, moulds, mildew, chemicals, and natural degradation. Nylon has potential uses in outdoor engineering applications upon coating with weather-resistant rubber.



**Figure 4.3** A Nylon fabric showing the weaving pattern

These man-made continuous filament fibres have mechanical characteristics such as high tenacity, high elongation at break, low modulus, excellent fatigue and abrasion

resistance, good impact resistance. These features enable appropriation for many industrial rubber-coated fabric/cord applications. These include: (i) high-pressure hoses, (ii) flat and vee-belts, (iii) conveyor belts and (iv) reinforcing tyre cords [10].

The advantage of using Nylon 6,6 instead of Nylon 6 is because of the higher melting point of the former (250 °C) compared with that of the latter (225 °C) which may facilitate the processing of the fibre at higher temperatures. To retain the dimensional stability during the use of a product reinforced with Nylon, the fabric should have been heat-set before rubberisation. The characteristics of Nylon are listed in **Table 4.2**.

<b>Table 4.2 Physical characteristics of different textiles</b>								
<b>Property</b>	<b>Unit</b>	<b>Cotton</b>	<b>Rayon</b>	<b>Nylon</b>	<b>Polyester</b>	<b>Aramid</b>	<b>Glass</b>	<b>Steel</b>
Moisture regain*	Percent	8.5	13	4.5	0.5	2.0	Nil	Nil
Tensile strength	MPa	230	685	850	1100	2750	2250	2400
Modulus	MPa	3.5	9	5.5	14	60	73	200
Elongation at break	Percent	8	10	16	14	4	5	2
Shrinkage at 150°C	Percent	0	0	5	11	0.2	0	-
Resistance to acid	-----	Poor	Poor	Good	Good	Very good	Very good	Good
Resistance to alkalis	-----	Good	Good	Good	Good	Very good	Excellent	Good
* Moisture absorbency difference in percentage at 21° C and 65 percent relative humidity (maximum)								



A very lightweight polyurethane-coated Nylon 6 fabric can be used for making sports garments, windcheaters, sleeping bags, swimwear, rain wear, and snow jackets.

#### **4.6.1 Characteristics of Nylon Fabric**

- Resilient and has high dimensional stability.
- High strength and excellent abrasion resistance.
- Low moisture absorption.
- Excellent elastic recovery and fatigue resistance.
- Resistant to many chemicals.
- Resistance to attack by insects, fungi, and rot.
- Low resistance to sunlight.
- Resistant to natural degradation.

#### **4.7 Polyester Fibre and Fabric**

Polyester fibre is produced from petroleum products. Polyester fibre is produced by reacting dicarboxylic acid with dihydric alcohol. The polyester fibres are melt-spun in a similar process to that used to make Nylon. The polyester fibres are hot-drawn to orient the molecules, so properties such as strength, elongation, and stress/strain are improved. The fibres retain the shape of the spinneret hole when they are melt-spun.

The basic polymer from which polyester fibres are made is polyethylene terephthalate (PET). The fibres have straight molecular chains that are packed closely together and are well-oriented, with very strong hydrogen bonds [2].

Polyester fibres can also be produced by remelting PET bottles as a recycling process, and fibres obtained by extrusion. PET is produced by reacting ethylene glycol with terephthalic acid or its methyl ester in the presence of an antimony catalyst. The reaction is carried out in a vacuum under high temperature to achieve the high molecular weights needed to form good quality fibres. It is then melt spun [8].

The basic polymer polyester enables the fibres to be modified physically and chemically, resulting in improved performance of the fibres. The fibre can be changed from the usual round shape to other shapes to obtain different properties. The properties of polyester fibre are detailed in **Table 4.1**.

Polyester fabric is a versatile and important synthetic fabric used in coating applications. It is strong and its texture is soft. Hence, it is suitable for use in making rubber-coated garments and technical textiles because the fabric is resilient and less likely to shrink.

High-tenacity polyester filament is available in the range of 6.8-9.5 g/denier and the elongation at break is 9–27%. These characteristics enable it to be used to make rubberised tyre cord and rubber-coated fabrics. If appropriate heat-set treatment is given to polyester textiles, they maintain the dimensional stability necessary to retain the dimensional appearance of the finished product. The physical characteristics of this fibre are detailed in **Table 4.2**.

Polyester fabrics have a high recovery rate with low elongation when compared with Nylon (which has better recovery at higher elongation). Hence, the former can be used in preference to rubber-coated textiles for making inflatable items. Higher-weight polyester is used for coating fabricated inflatable items of higher breaking strength. It is treated before coating with appropriate bonding agents to develop adhesion with the rubber coating.

This fabric is resistant to most chemicals, wrinkling, mildew attack, sunlight and the weather, and does not absorb much moisture from the atmosphere. It is also possible to produce high-tenacity staple polyester which can be blended with natural fibre cotton and Rayon to improve strength and absorbency if these properties are needed for making polymer-coated fabric for protective gear.

Polyester textiles can be used by applying a very thin coating with liquid polyurethane for making sportswear and rainwear.

The excellent resiliency of polyester and its dimensional stability after heat-setting make this material an important technical fibre for various industrial uses. Because of its versatility, polyester fabric has become the most widely used synthetic fibre in coating applications because the staple form can be blended with several fibres to provide the desired technical properties.

This fibre can be produced in different types. Filaments may be high or regular tenacity in a white colour or can be solution dyed to get the desired colour shade of the fibres. Usually, the fibres are rod-like and smooth-shaped with a circular cross-sectional structure. However, different cross-sectional shaped polyester fibres can be produced to meet the various industrial applications if they are coated with elastomers [6].

The strength and abrasion resistance of polyester fibres is excellent. Increased fibre strength can be produced by hot-drawing to develop crystallinity and by increasing the molecular weight. They have very good resistance to UV light and low moisture

absorbency (0.4-0.8%). To improve the breathability of polyester when a coated fabric is used for protective garments, blends with absorbent fibres such as cotton are used to absorb body moisture and thus provide comfort for the user.

The development of a new polyester in industrial applications, polyethylene naphthalate (PEN; Shell Chemical Company) has led to its use in elastomer coatings for making industrial rubber hoses, rubberised tyre cords, and rubber belts. The modulus (measurement of resistance to deformation of fibre) of PEN fibre is about five-fold higher than that of Nylon and 2.5 times that of polyester. It has low elongation, low shrinkage, with very good dimensional stability [7].

#### **4.7.1 Characteristics of Polyester Fabric**

- Strong, stretchable, resilient, and durable.
- Resistant to creasing, shrinkage, and wrinkling.
- Abrasion resistance is high.
- Resistant to most chemicals, mildew, sunlight, and the weather.
- Very low moisture regain.
- Can be blended with other fabrics to increase physical properties.

#### **4.8 Kevlar**

Kevlar (poly-paraphenylene terephthalamide [PPTA]) is the trademark for a light, strong para-aramid synthetic fibre. It is spun into fabric sheets used as reinforcement in composite materials when coated with elastomers. This advanced material is lightweight yet has high strength and can provide protection on extreme impact. A Kevlar fabric swatch is shown in **Figure 4.4**.

Kevlar is synthesised in solution from the monomers 1,4-phenylene diamine and terephthaloyl chloride in a condensation reaction and yields hydrochloric acid as a by-product.

Kevlar production is expensive because of the difficulties arising from using concentrated sulfuric acid needed to keep the water-insoluble polymer in solution during its synthesis and spinning.

Kevlar consists of long molecular chains produced from PPTA. There are many inter-chain bonds which make the material extremely strong. Kevlar has relatively rigid molecules which tend to form mostly plain sheet-like structures.

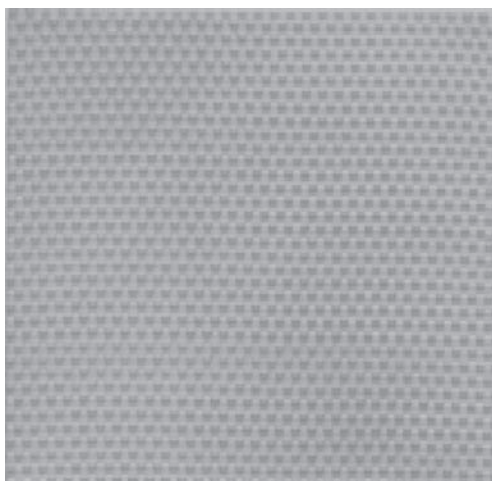
This polymer has very good resistance to high temperature and can maintain its strength and resilience at a cryogenic temperature of  $-196^{\circ}\text{C}$ . At higher temperatures, the tensile strength is reduced by 1-20% upon long duration; the strength reduction is ~50% if it is exposed at  $260^{\circ}\text{C}$  for 3 days.

Aramid (aromatic polyamide) long-chain continuous filament yarn exhibits very high tenacity and the lowest elongation at break of textile yarns. It is used in very high-strength rubber-coating applications such as radial tyres, as well as for inflatable devices for military and mechanical applications. There are three grades of Kevlar used as reinforcement in these products. Kevlar29 is lightweight and is suitable for bullet-resistant undervests. Kevlar49 has very high tenacity and is used as reinforced fibre in elastomer composites for automobiles, boats, aircraft, and aerospace vehicles. Rubber-coated Kevlar can be used instead of traditional steel components in the manufacture of tyres because of its strength-to-weight ratio. This causes significant changes to its properties: very lightweight, lower rolling resistance and better fuel consumption. The comparative stress-strain behaviour of aramid fibres is demonstrated in **Figure 4.7**.

This material is well known as a component of vests that protect against bullets and sharp objects. It can be thinly coated with rubber for such important applications. Rubber-coated Kevlar is used as an inner lining for some bicycle tyres to prevent punctures. Elastomer-coated Kevlar can be used for safety clothing for motorcyclists (especially in areas featuring padding on highly abrasive surfaces).

Upon rubber coating, it can be used on the vamp area of rubber footwear to prevent chainsaw injuries. The rubber-coated Kevlar fabric can be utilised as a reinforcing material for making rubber bellows, expansion joints and for other engineering applications. This high-strength coating is used to reinforce rubber hoses used in high-temperature applications. Kevlar in cord form can be used as an outer covering of rubber braided hoses, and on coating the braided outer, it provides high protection against cuts from the sharp objects and can protect the hose from damage if it is dragged on highly abrasive surfaces.

The physical characteristics of different fibres are shown in **Table 4.2**.



**Figure 4.4** Kevlar fabric

A *meta*-variant of the *para*-aramid Kevlar has the trade name Nomex. It was introduced by DuPont for use in heat- and flame-resistant applications. Kevlar has a *para*-orientation so the molecules can be aligned and high strength obtained. However, *meta*-aramid polymers cannot align during filament formation and so have poor strength. Polymer-coated Nomex can be used in protective gear, which can offer high heat resistance, flame-retardancy with low smoke generation, and be used for environmental protection.

Aramid fibre composites coated with polymers can be widely used in combination with carbon and glass fibre in military and other technical uses. Its major disadvantage of low elongation occurs if the aramid is used in several layers.

Ultra lightweight car tyres have been developed by Dunlop using Kevlar (DuPont) fibres which are claimed to be five times stronger than steel. Replacing the conventional steel components (usually implemented for producing tyres on rubber coatings in sequence to reduce fuel consumption) improved the performance of the tyres [11].

#### **4.8.1 Properties of Kevlar Textiles**

- High tensile strength at low weight.
- Excellent dimensional stability.

- Low elongation at break.
- High modulus and toughness.
- Flame-resistant, self-extinguishing.
- High chemical resistance.
- Low electrical conductivity.
- Low thermal shrinkage.
- High cut resistance.
- Degrades under UV light.

To quickly identify the presence of some of the synthetic fibres, the burn test can be used. The burn test may not be acceptable for blends of fibres and for the fibres which have been treated for flame retardancy. Solubility tests are the appropriate procedure for differentiating synthetic fibres [4]. A graphical representation of the limited oxygen index (LOI) of different fibres is shown in **Figure 4.18**.

## **4.9 Carbon Fibre**

Carbon fibres are essential for the aerospace industry, particularly for defence aircraft where lightweight and high-strength materials are in great demand. The typical diameter of carbon fibre is  $\sim 7\ \mu\text{m}$  and the tensile strength is  $\leq 22,000\ \text{MPa}$ . Polymer composites of carbon fibre matrices are most suitable if lightweight, very high strength, and exceptionally good fatigue characteristics are important requirements. Carbon fibres with elastomer coatings can perform well when high temperature resistance, chemical inertness and high damping properties are the major criteria. Various properties of carbon fibre are detailed in **Table 4.1**.

These fibres are prepared by heat-treating organic textile fibres by stripping off the side chains, leaving only the carbon backbone. The latter is subjected to further consecutive heat and mechanical treatment such that the crystallite are oriented along the axis of the fibre.

Carbon fibres which contain  $\geq 90\%$  carbon are obtained by the controlled pyrolysis of appropriate fibres. Carbon fibres which contain  $>99\%$  carbon are called 'graphite fibre'. Various types of carbon fibres with different morphologies and specific characteristics are obtainable from various precursors. The most prevalent precursors are: polyacrylonitrile (PAN); cellulosic fibres (viscose Rayon, cotton); petroleum or coal tar pitch; and certain phenolic fibres.

The most popular precursor of modern carbon-fibre manufacture is PAN fibre because it has the following advantages: (i) high degree of molecular orientation (ii) higher melting point (iii) greater yield of carbon fibre.

Carbon fibres are produced by the controlled pyrolysis of organic precursors. The precursor removes the oxygen, nitrogen, and hydrogen to form carbon fibres. The mechanical characteristics of the carbon fibres are improved by increasing crystallinity and orientation, and by reducing defects in the fibre. One must start with a highly oriented precursor and then maintain the initial high orientation during stabilisation and carbonisation through tension of the fibres [12]. The conversion of PAN precursors into high-performance carbon fibres involves these stages:

(i) **Oxidative stabilisation** – the polyacrylonitrile precursor is first stretched and simultaneously oxidised at 200-300 °C. This treatment converts thermoplastic PAN to a non-plastic cyclic or ladder compound.

Conversion of PAN fibres into carbon fibres involves treatment of the fibres in an oxidising atmosphere at 200-300 °C while the fibres are in tension (which prevents shrinkage or extension of the fibres).

(ii) **Carbonisation** – after oxidation, the fibres are carbonised at ~1000 °C without tension in an inert atmosphere (usually nitrogen) for a few hours. During this process, the non-carbon elements are removed as volatiles to give carbon fibres with a yield of ~50% of the mass of the original PAN.

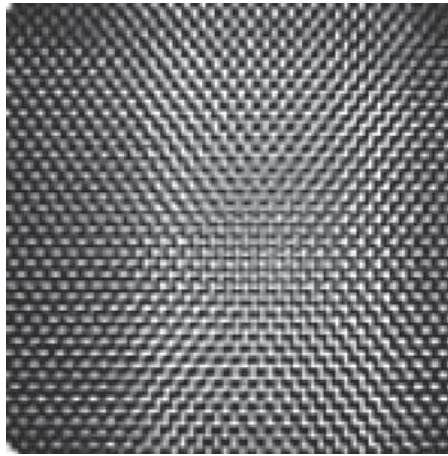
(iii) **Graphitisation** – fibres are treated at 1500-3000 °C depending on the type of fibres required, this improves crystallite orientation in the direction of the fibre axis.

The conversion of Rayon fibres into carbon fibres involves the process phase described next.

- Stabilisation is an oxidative process that has a number of steps. In the first step (at 25-150 °C) is the physical desorption of water. The second step (at 150-240 °C) is dehydration of the cellulosic unit. The final stage is the thermal cleavage of the cyclodidic linkage, scission of ether bonds, and scission of some C–C bonds via a free-radical reaction at 240-400 °C, when aromatisation occurs.
- Carbonisation occurs at 400-700 °C. The carbonaceous residue is converted into a graphite-like layer.
- Graphitisation is carried out under strain at 700-2700 °C to obtain high modulus fibres through the longitudinal orientation of the planes.

The strength of a carbon fibre is dependent upon the:

- Type of precursor
- Condition of processing
- Heat-treatment temperature
- Flaws and defects in the fibre



**Figure 4.5** Carbon fabric

It is postulated that the higher the tensile strength of the precursor, the higher the tenacity of the carbon fibre. If moderate stabilisation is used, the tensile strength and modulus are significantly improved by carbonisation under strain. The strength increases up to a maximum of 1300 °C with PAN-based carbon fibres. It then decreases with increasing temperature, and the modulus increases. Carbon fibres are brittle; the layers in the fibres are formed by strong covalent bonds. Sheet-like aggregations allow easy crack propagation. On bending, the fibre fails at very low strain [13]. Carbon fabric is shown in **Figure 4.5**.

Because of its very high cost, the application of carbon fibres for rubber coating as reinforcing material is restricted to exceptionally specialised fields. Its tensile strength can be compared with that of glass fibre reinforcement ( $\leq 220,000$  MPa). The modulus of carbon fibre is five-fold greater than that of high-tensile steel and six-fold higher



than that of glass, hence applications may be necessary in certain specific and highly demanding areas. The comparative properties of carbon fibre with other fibres is given in **Table 4.1**.

#### **4.9.1 Characteristics of Carbon Textiles**

The characteristics of carbon textiles are:

- High strength, high modulus, tough and lightweight.
- Very high temperature resistance.
- Excellent dimensional stability.
- Outstanding resistance to fatigue, abrasion and corrosion.
- Excellent resistance to chemicals, acids, alkalis and solvents.

#### **4.10 Glass Fabric**

Fibre glass is an inorganic substance. The textiles are made from extremely fine fibres of glass. This fabric is used as a reinforcing agent in the production of elastomeric-coated textiles. The resulting composite is effective in heat- and flame-resistant applications.

Glass fibre is formed when thin strands of silica-based glass are extruded into numerous fibres of minute diameter. Glass is unlike other polymers; it has little crystalline structure even as a fibre, and can be considered to be ‘frozen’ in its amorphous stage. The properties of the structure of glass in its softened stage are very much like the properties when it is spun into fibres. Glass textiles do not burn, so they can be used in fire-resistant and very high heat-resistant applications [14]. The properties of glass fabric are listed in **Table 4.2**.

The raw materials for glass are sand, silica, and limestone. These are combined with additives such as feldspar and boric acid. These materials are melted in large electric furnaces at 1300 °C. Holes are provided at the base of the melting chamber for making filament yarn. Molten glass flows through the holes, and is carried to a winder installed below the chamber. The winder rotates at high speed; this stretches the fibres and reduces their size before the fibres become hard.

To produce glass fibres in staple form, the glass flows out from the holes fitted in the base of the furnace in thin streams. Breaking of the strands is achieved by using jets of high pressure air or steam so as to acquire strands of length 20-25 cm. A thin

snare is collected on a rotating drum, and soft, untwisted yarns are produced. The prepared glass fibres can be woven into fabric for coating with polymers.

Industrial glass fabric can be produced in different weave patterns:

- Plain weave has an inseparable structure with plain clear lines.
- Twill weave is of high density. A soft and structural weave is used mainly as a reinforcing material.
- Satin weave is of high density. It is a soft and loose-structure weave, with good texture. Used as highly reinforcing coated material.

Glass has a specific gravity of 2.48 to 2.69, so it is very heavy. It has a tenacity of 9.6 g/d with low elongation (3-4%) with very good elasticity. It tends to be brittle and break when bent, exhibiting poor flex resistance to abrasion. However, these properties can be improved if the textile is coated with a flexible matrix of elastomers.

Glass fabric is non-absorbent, and resistant to sunlight and most chemicals. This fibre is flame-proof, so can be safely used with flame-resistant rubber coatings. A sample of glass fabric used for rubber coating is shown in **Figure 4.6**.

The vitreous and crystalline states of silica, glass and quartz, respectively, have similar energy levels on a molecular basis. This implies that the glassy form is extremely stable. To induce crystallisation, it must be heated to >1200 °C for long periods of time.

Although pure silica is a perfectly effective glass fibre, it must be worked at very high temperature: this is a problem unless its specific chemical properties are needed. A new type, E-glass, has been developed that is alkali-free (<2%) and is an aluminoborosilicate glass (the first glass formulation used for continuous filament formation). This category of glass is still in use for producing most of fibre glass [15].

The purpose of using the letter 'E' is because E-glass was originally intended for electrical applications. Another type is S-glass, which is a high strength formulation if tensile strength is the most important prerequisite. Similarly, C-glass was developed to resist attack from chemicals (primarily the acids that affect E-glass).

Two main methods are followed to manufacture fibre glass materials:

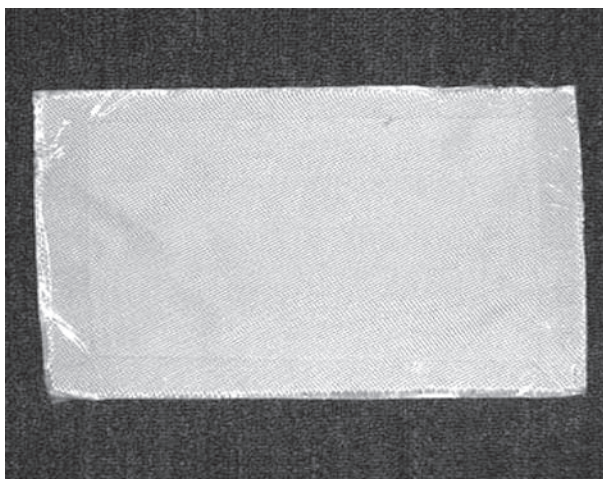
- Direct melt process
- Marble remelt process

The materials are mixed together and melted in a furnace. After the marble process, the molten material is sheared and rolled into marbles, which are cooled and stored.

They are remelted again and molten glass extruded to the bushing for fibre formation. In the direct melt process, the molten glass in the furnace goes right to the bushing for formation. The bushing plate is made of platinum alloy with rhodium for durability. The metal furnace contain nozzles to form the fibre.

In this process, the bushing serves as a collector for the molten glass, it is heated slightly to keep the glass at the correct temperature for fibre formation. The bushing acts more like a furnace in the marble melt process because it melts more of the material. The number of nozzles ranges from 200 to 4,000 in multiples of 200. The basic fibre thickness of glass fibres is maintained at 9  $\mu\text{m}$ . It is important to maintain the drawing speed. Coarser fibres may be produced by slowing down this speed. Also, it is uneconomical to run at speeds for which the nozzles are not designed.

Controlling the viscosity of the molten glass is essential. The viscosity should be relatively low during drawing (pulling of the glass to reduce fibre circumference). Too high a viscosity will break the fibre during drawing; if it is too low, the glass will form droplets rather than drawing out into a fibre [16].



**Figure 4.6** Glass fabric for coating

Rubber-insulated fibre glass is utilised as mats, insulation, reinforcement, heat-resistant fabrics, corrosion-resistant fabrics and high strength fabrics.

Glass fibres are useful for coating applications because of their high ratio of surface area to weight. The fabric/coating ratio in coating applications is maintained similar to that for fibres of organic origin (i.e., 30 and 70). However, the increased surface makes them much more susceptible to chemical attack. Glass has an amorphous structure, so its properties along and across the fibre are identical. Humidity is an important factor with respect to tensile strength. Moisture is easily adsorbed, and can worsen microscopic cracks and surface defects, and lessen tenacity [15]. In contrast to carbon fibre, glass can undergo more elongation before it breaks. The stress-strain behaviour of glass fibre is shown in **Figure 4.7**.

#### **4.10.1 Characteristics of Glass Fabric**

The characteristics of glass fabric are:

- Incombustibility.
- Resistance to most acids and alkalis.
- Resistance to high temperature.
- Electrical resistance.
- Non-degradable; can be used in geotextiles.
- Excessively brittle.

#### **4.11 Asbestos Fibre**

Asbestos is a fine, fibrous material. One variety of this fibre is softer and can be woven; it is available at a length of 60 cm, has high tensile strength, and provides very low extension. The largest producer of asbestos ( $\leq 80\%$  of total consumption in the world) is Canada. The yarn can be spun from long fibres and woven to make fireproof clothing and heat-insulating materials. It is composed of fibrous silicate minerals (mainly calcium silicate and magnesium silicate).

Asbestos woven cloth is used for making high heat-resistant/flameproof rubber hoses, heat-insulating coated material, and rubber asbestos composites for brake linings.

Its use has been restricted because the handling of short fibres may cause asbestosis [17].

#### **4.11.1 Characteristics of Asbestos Fabric**

- Very high tensile strength.
- Low extension.
- Very high heat-resistance (melts at 1550 °C).
- High electrical resistance.
- Inertness to chemicals.
- Not resistant to mineral acids (dissolves in sulfuric acid).

#### **4.12 Steel Fibre**

Steel cord is used to reinforce rubber-made items such as conveyor belts, radial tyres, and hoses. To obtain adequate bond strength with the composition of steel and rubber covering, the steel cords are zinc-coated. In addition, suitable additives must be incorporated into the rubber compound for good adhesion.

The twisted steel cords should have the equal diameter and pitch comprising alternate twists of Z and S so that the end-product (a belt) can run straight. To get the desired belt strength, the correct combination of cord diameter and number of cords is important.

Steel-cord rubber belting is widely used in the mining industry to carry coal and other minerals from the mines. To reinforce rubber belting, the steel is drawn to a specific diameter to make cords. The basic construction of steel cords should be in a straight line in a plane embedded in rubber. To achieve improved adhesion with rubber and to prevent corrosion, the steel cords are coated with zinc or brass (a brass coating is applied for small-diameter cords).

The main purpose of using steel cord in rubber products is to obtain very high strength with low extension and good flexibility. The physical attributes of steel fibre (along with comparison with other fibres) are shown in **Table 4.1** and **Table 4.2**.

The quality of steel fibre is dependent upon the properties of the raw materials and the technology used for producing it. Rolled wire of diameter 5.5-6.5 mm is used as a basic semi-product treated by mechanical, thermal and chemical processes. In mechanical processing, gradual thinning of the fibre is by drawing through hard metal dies of reduced dimension. After each drawing, the fibre is subjected to chemical treatment. Just before the final drawing, the fibre is coated with zinc (70%) and copper (30%),

to obtain good rubber-steel adhesion and corrosion prevention, respectively. The steel fibres can be made with a diameter of 0.15-0.30 mm. On gradual reduction of the thickness, the fibre's resistance to repeated strain in bending increases markedly but the resistance to its mutual abrasion in cord decreases. Making cords from steel fibre by roping is similar to the twisting of textile fibres [18]. Varying the thickness of the basic fibre and variation of the cord threads gives different strengths to the end material.

Steel cords can be made into fabrics. Woven steel fabric made of steel warp and weft with a brass coating has a thickness of 3-6 mm and a breaking strength of 350-1600 kN/m. It provides high impact resistance, good adhesion with rubber, as well as good tear and impact resistance.

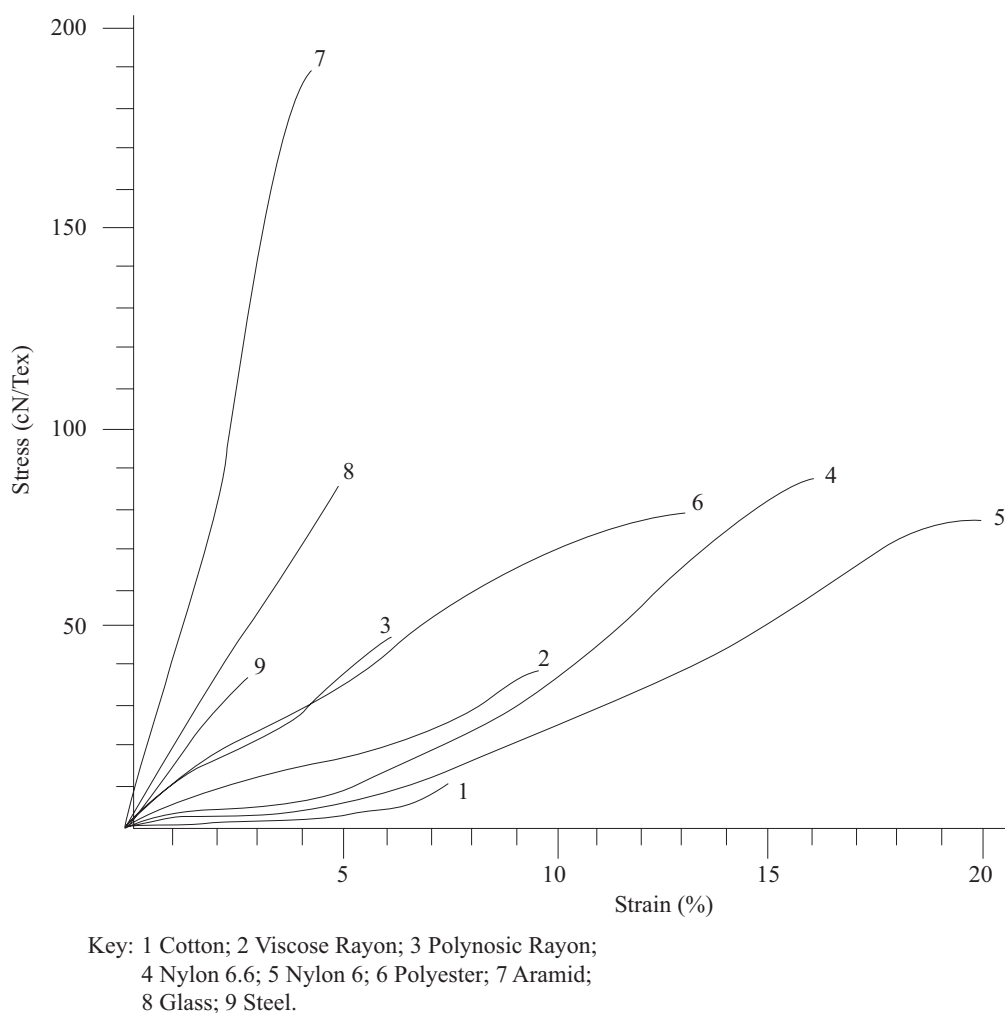
Steel cords are available as spools of different weight according to requirements. The spools can be used directly for rubber-coating processes.

There is growing demand for steel cord because of the increasing demand in radial tyres, for applications such as conveyor belts, and for use in high pressure steel cord-braided rubber hoses [19]. The stress-strain behaviour of steel is shown in **Figure 4.7**.

#### **4.12.1 Characteristics of Steel Cord**

The characteristics of steel cords are:

- Very high strength
- Excellent dimensional stability
- Good flexibility
- Low extension
- Excellent fatigue resistance
- Very good impact resistance
- Excellent tear resistance



**Figure 4.7** Stress-strain characteristics of textile fibres. Reproduced with permission from D.B. Wootton, *The Application of Textiles in Rubber*, Rapra Technology, Shrewbury, UK, 2001. © Rapra Technology, 2001

### 4.13 Construction of Textile Fabrics

Textile fibres produced in an original form have very limited use in rubber. To obtain the best characteristics as reinforcing components in polymeric coatings, the textile yarns must be constructed correctly.

#### **4.13.1 The Fibre**

Fibres of natural or synthetic origin should have a high length-to-width ratio with appropriate properties for the constitution of the textile fabric.

A simple yarn is smooth and uniform. It is evenly twisted, composed of two or more single fibres twisted together. The fineness and amount of twist are the important properties of a yarn. If more twist is applied to a yarn, it becomes finer, smoother and stronger.

The yarns are a collection of fibres twisted (twirl arrangement of fibres around the yarn axis) together to form a continuous thread. They are used in the construction of textile fabric. Filaments are long fibres, and the spun yarn is a continuous strand of staple fibres held together. Depending upon the length of fibre, a yarn can be drawn as a filament or spun yarn. It can also be described by the amount and direction of twist and the size of the yarn. The direction of the twists of the yarns is shown in **Figure 4.9**.

Based on the length of fibre, a simple yarn can be turned as a filament or spun. Filament fibres and filament yarn size are indicated as weight per unit length. To express this, the ‘denier’ (weight in grammes of 9,000-metre length) is applicable for fibres and yarns.

The yarn can be classified as single, ply or cord yarn. A simple form of a yarn having only one strand is called a single-end yarn. A ply yarn can be prepared by applying a second twist (the helix assembly of fibres around the axis of the yarn) to a simple yarn. It enhances the uniformity, diameter and strength on plying the yarn, thereby improving the quality. The amount of twist may vary according to the size and length of the fibres, and the purpose of the end use. To increase the strength of the woven fabric, ply yarns may be used in a warp direction during weaving.

#### **4.13.2 Cords**

A cord can be prepared by applying a third twist on the twist ply yarns. Cord yarns are utilised for making industrial fabrics and higher-weight fabrics such as canvases used for coated material with a high ratio of weight/strength.

A single-end cord is constructed from several yarns twisted together. For the manufacture of rubber hoses and rubber transmission ‘V’ belts, several yarns are twisted together to form a single-end cord, which provides reinforcement to the product. Similarly, single-end reinforcement cords are assembled together into a



cord-fabric which is then rubberised and used in the construction of tyres. Making use of tyre cord which provides strength in the warp direction, and the weft which holds the cords in position, facilitates rubberisation during calendering.

A cord comprises two or more ply yarns held together by twisting. Preparation of a cord involves using yarns in a bundle and twisting them separately; the yarns are then twisted in the opposite direction. To obtain thicker material, similar assemblages can be twisted together to make a large corded structure; this can be repeated to make a rope [20]. Yarn, ply yarns, and cords are shown in **Figure 4.8**.

A cord may be described as being '2/1650 denier'. This means that two yarns of a bundle of continuous filaments adding up to 1650 denier form a cord upon twisting collectively. The thickness of filament fibres is denoted by 'denier' (i.e., a 9000-metre long single yarn, weighing 1650 g). Such cord can be used in rubberisation to fabricate articles such as rubber belts.

The denier number is smaller, which means that a thinner filament is employed. Hence, the thickness of the yarn that is produced will also be reduced [21].

#### **4.13.3 Textiles**

The most effective form of reinforcement provided with textiles in polymer composites is by woven fabrics.

A satisfactory form of textile reinforcement used for various technical and general purposes is of woven construction. Most of the elastomeric coatings provided on woven fabrics are inflatable products, personal protective garments, and healthcare products. If employed in elastomeric coatings, a woven fabric or 'textile' is taken up as a constructional reinforcement of the end product. However, steel and glass are usually not categorised as textiles. Upon use of rubberised woven fabrics in industrial applications, the warp is stronger than weft because the former carries the major stress (e.g., rubberised conveyor belts and flat transmission belts).

Yarns must be assembled together into a consistent form in various industrial applications of rubber textile composites. In certain special applications, coatings may be necessary for use in non-woven and knitted fabric construction. This provides specific advantages to the end product (e.g., military protective garments, inner lining of rubber footwear).

The 'yarn count' is the number of times a standard length is contained in 1 lb. For example, a cotton cord can be illustrated by the code 25<sup>3</sup>/4/3. This indicates that four

single yarns, each of 25<sup>s</sup> count, were twisted together to form a thread, and that three of such threads were combined to form the cord. In woven fabric, the count is also assigned to yarns per inch in the warp and filling direction.

The strength of yarns, threads or cords can be expressed as the load (in kg) necessary to break them. However, for simplicity of assessment, its ‘tenacity’ can be precisely resembled. This is the breaking load (expressed in g per denier) of the yarn. For example, for a 2/1600 denier cord breaking at a load of 14 kg, its tenacity is just 4 g/denier [22]. The tenacity of various fibres used for elastomer coatings is illustrated in **Table 4.1**.

The calculation of denier, tex, dtex, and tenacity of yarns/fibres is expressed as follows:

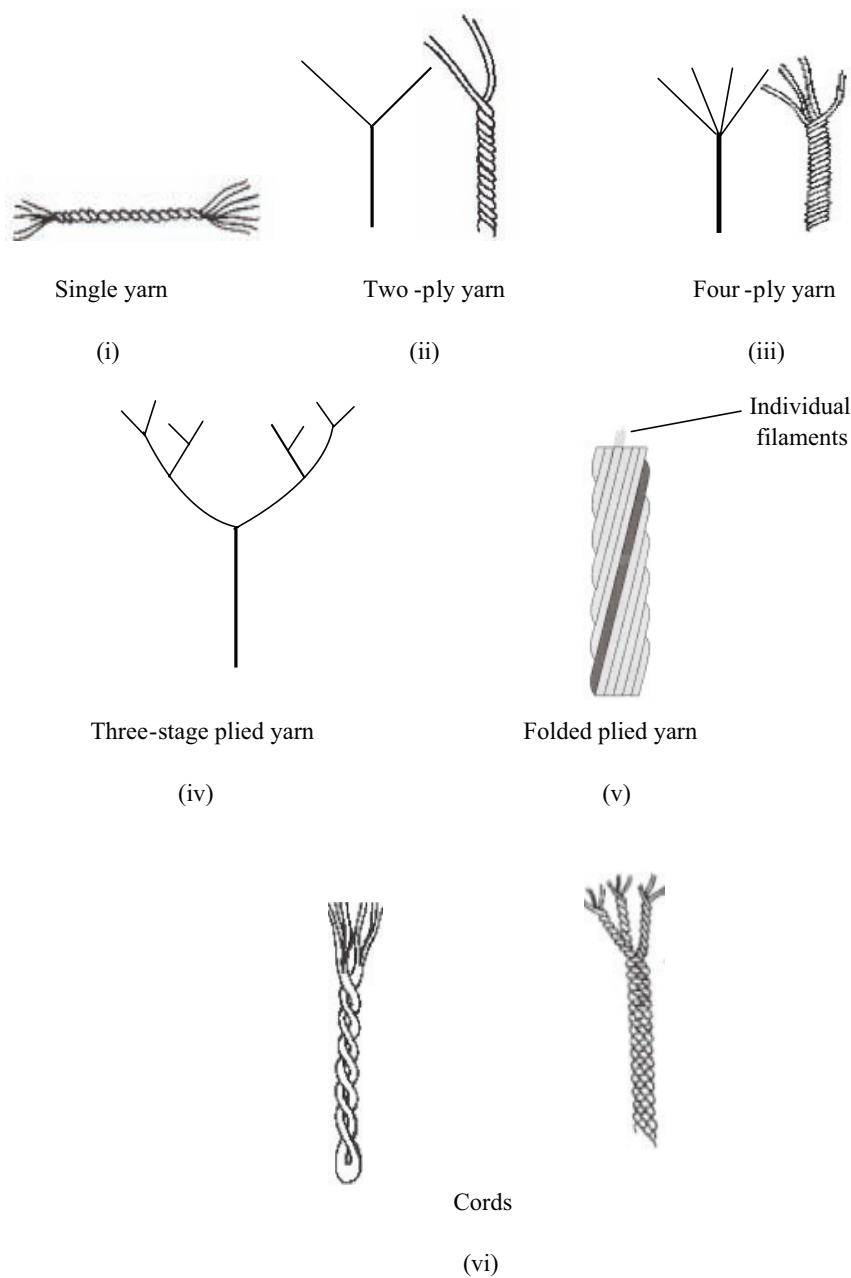
$$\text{denier} = \frac{\text{weight of a piece of yarn (in g)}}{\text{length of the piece of yarn (in m)}} \times 9,000$$

$$\text{tenacity (in g/denier)} = \frac{\text{strength (in g)}}{\text{denier}}$$

A tex is a measurement of the linear density of a yarn or cord. It is the weight in grammes of a 1000 m length; a decitex (dtex) is the weight in grammes of a 10,000 m length [23].

$$\text{One tex is equal to 0.11 denier (tex)} = \frac{\text{denier}}{9}$$

$$\text{dtex} = \frac{\text{weight of a piece of yarn (in g)}}{\text{length of the piece of yarn (in m)}} \times 10,000$$



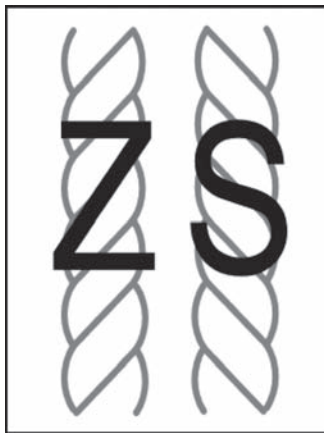
**Figure 4.8** Ply yarns and cords. Figure (v) reproduced with permission from D.B. Wootton, *The Application of Textiles in Rubber*, Rapra Technology, Shrewbury, UK, 2001. © Rapra Technology, 2001

## **4.14 Weaving of Textiles**

Textiles are woven by hand or machine. Most textiles are produced by twisting fibres into yarns and then knitting or weaving the yarns in construction of the fabric.

### **4.14.1 Spinning**

Fibres are twisted in the spinning process so that yarn breakage can be prevented when it is under tension. This process involves a spiral arrangement of the fibres around the axis of the yarn, which is made by rotating one end of a fibre strand while holding the other end still. The twisting of the yarn may be undertaken in each of two directions termed Z-twist or S-twist. In weaving yarns, the Z-twist is more common than the S-twist. A single yarn or fibre runs parallel at an angle stroke of the letter Z. In the case of the S-twist, the fibres or yarns run parallel to the angled stroke of the letter S. Depending on the length of fibres, the amount of twist varies with the size of the yarn and its ultimate use. The directions of the yarn twists are shown in **Figure 4.9**.



**Figure 4.9** Z-twist and S-twist of yarn

The 'twist' is specified by the number of turns per unit length, such as turns per inch (tpi) or turns per metre. Increasing the amount of twist to the point of perfect fibre-to-fibre consistency enhances yarn strength, but excessive twist positions the fibres at right angles to the yarn axis. This may cause a shearing action among fibres and may

affect the strength of the yarn. Nevertheless, the performance of the product and the cost of the yarn is dependent upon the number of turns [4].

The fibres making up a yarn may be continuous filament fibre (e.g., synthetic filament) or they may be staples of a few centimetres in length. Fibres usually vary from 12.5 mm to 62 mm in length.

#### **4.14.2 Spun Yarns**

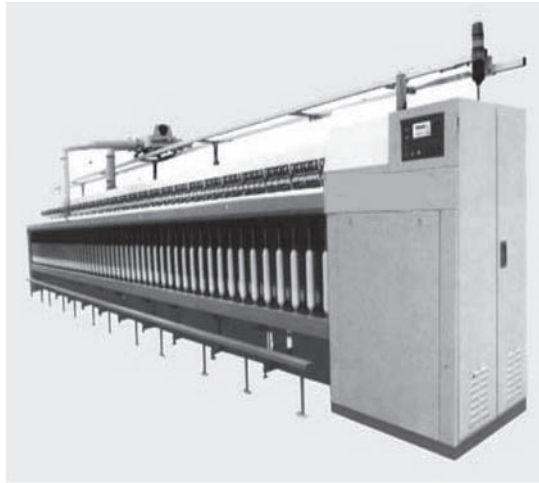
Spun yarns are continuous strands of short-staple fibres that are twisted together or that are spun to produce yarns with protruding fibre ends. Longer-staple fibres can produce good-quality spun yarns. The twist binds the fibres together and contributes strength to the spun yarn. To determine the strength of the spun yarn against breaking, the primary requirements for the technical preparation of the fabric intended for coating are the amount of twist, the length of the fibres, and the thickness of the yarn.

Natural fibres (except silk) are available in the form of fibres. Cotton is available in short lengths (12.5-50 mm) but animal-originated fibres such as wool are much longer (50-300 mm). Synthetic fibres are manufactured in continuous filaments. With respect to elastomeric coating, the continuous filament can be cut into staple fibre form, and a yarn can be spun.

The purpose of making spun synthetic fibres for textiles instead of smooth and polished surfaces using continuous filament is to improve adhesion during rubberisation because the protruding ends provide mechanical anchorage with the substrate.

In processing spun yarns, 'roving' is a step to reduce the size of 'sliver' (a rope of fibres produced as intermediate steps during the processing of spun yarns) and the fibres can be made more parallel by inserting an amount of twist. A roving frame is shown in **Figure 4.10**.

With the application of more twists, the strength of the yarn can be increased by employing longer fibres and thicker yarns. Thinner yarns require more twist than their thicker counterparts to increase the resistance to break when under stretch. Along the length of a yarn its thickness may vary. A 'slub' is a much thicker segment in which a mass of fibres is integrated into the yarn. Synthetic polymer fibre-type spun fibres are chemically different from the original polymers [8].



**Figure 4.10** Cotton spinning machine: roving frame

#### **4.14.3 Weaving**

Woven fabrics are made of two sets of yarns: a length-wise set called the ‘warp’ and a crosswise set called the ‘weft’. Warp yarns are threaded into a loom through a series of frames called ‘harnesses’.

Weaving is the art of producing textiles where two distinct sets of yarns, the warp and weft (or filling), are interlaced at right angles to each other. The warp and the weft form a fabric. The warp threads run lengthways through the piece of textile, and the weft runs across from side to side. The manner in which the warp and filling threads interlace with each other is known as the ‘weave’.

During the process of making a fabric, the harnesses raise some warp yarns to others, and this action creates a space or ‘shed’ between the yarns. The weft thread is wound onto spools called ‘bobbins’, and are placed in a ‘shuttle’, which carries the weft thread through the shed. The shuttle carries the filling yarns through the shed, and forms the crosswise yarns of the fabric. The harnesses which are raised for each pass of the shuttle have a specific pattern, and this movement determines the type of weave.

The raising and lowering sequence of warp threads gives rise to many possible weave structures from simple *plain weave*, through *twills* and *satins* to complex computer-generated interlacings.

Most woven products employed in coating purposes are commercially available with one of these basic weaves: (i) plain (ii) twill or (iii) satin. Upon coating with rubber, items can be fabricated and utilised for technical, industrial, and personal protection items [24].

#### **4.14.4 Loom-weaving**

Weaving is undertaken on a machine called a ‘loom’. It is a device that weaves cloth. The basic purpose of any loom is to hold the warp threads under tension to enable the interweaving of the weft thread.

All the weaves that are used today have been made for centuries. The earliest looms were made of wood: vertical-shaft looms with ‘heddles’ fixed in the shaft. Each thread in the warp passes through a heddle (which separates the warp threads for the passage of the weft). Heddlers are made of wire or cord. The vertical space between the raised and non-raised yarns in the warp direction is called a ‘shed’.

Looms have undergone significant improvement, but the elementary functions are identical to those used for centuries. Warp yarns are held taut within the loom, and filling yarns are inserted and pushed into place to produce the fabric. Filling yarns are inserted by a shuttle battled through raised warp thread. To separate the warp yarns and weave faster, alternate warp yarns are attached to bars that raise the alternate warp yarns.

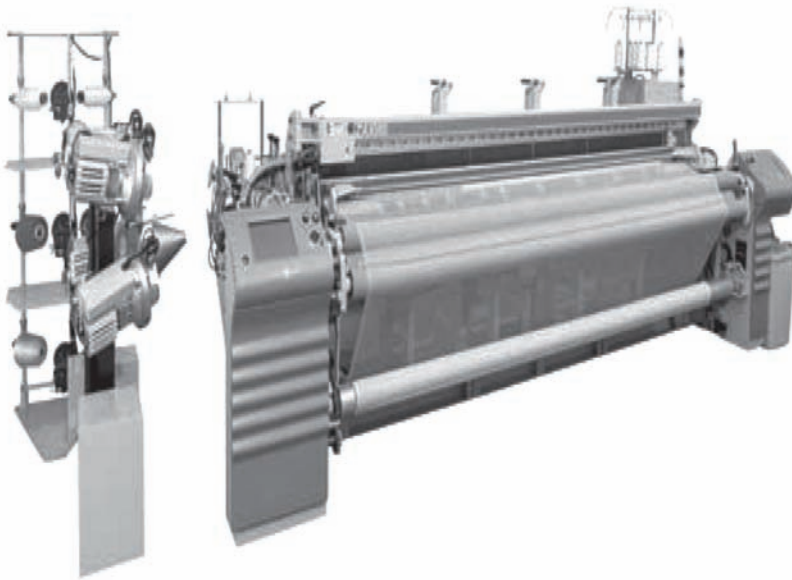
The developments that have taken place on shuttle-less looms have been to: (i) increase productivity; (ii) increase the flexibility of the looms to weave different kinds of fabric; (iii) reduce the amount of down time; (iv) develop accessories; and (v) introduce electronic control systems to increase automation.

While weaving technical textiles, the weft is suitable to carry air jets. The process uses carefully controlled, rapidly moving jets of air. In this loom, a pre-measured filling is guided through a nozzle, where a narrow jet of air sends it through the shed at high speed.

The loom can operate at a speed up to 1000 picks per minute. This can be undertaken for spun filling yarns provided they are lightweight.

Lighter fabrics are very difficult to control through the shed; yarns that are too heavy cannot be carried across the loom by an air jet. Despite these limitations, air-jet looms can produce a wide variety of fabrics.

Air-jet looms are recommended for producing tyre cords and glass fibre fabrics. A modern air-jet loom is shown in **Figure 4.11**.



**Figure 4.11** Air-jet loom

One type of highly efficient loom used for weaving synthetic textiles is the water-jet loom. In this loom, a high-pressure jet of water carries the filling yarn across the warp. This loom is suitable for Nylon and polyester filament yarn fabrics, and excess water is removed from the loom by suction.

This device can operate two to three times faster than conventional looms. Compared with conventional looms, water-jet looms can provide 400-600 picks per minute; have lower power consumption; have low noise; and can operate at a lower cost of production. Automation of water-jet looms reduces machine vibration.



The fabric is wet during weaving. Thus, there is a possibility of attack by mildew upon storage and impairment to adhesion during coating. It is therefore necessary to dry the fabric to avoid these problems.

The pick is tension-free, so a very high quality of warp yarns are needed for efficient operation. Yarns that are not readily absorbent can be used to make fabrics on water-jet looms (e.g., Nylon, polyester, glass). These machines can produce very high-quality fabrics having a good appearance and feel.

Water-jet-loom products are suitable for use in making air-bag coatings as well as rubberised products if flat yarns are used [25]. A water-jet loom is shown in **Figure 4.12**.

Another device employed to weave synthetic textiles is the projectile loom. In this machine, one projectile with grippers carries the yarn across the full width of the shed, and the yarn can be inserted from one or both sides.

This loom is also called a ‘missile loom’ because the picking action is done by a series of small, bullet-like projectiles which hold the weft yarn and carry it through the shed and then return empty. A special ‘tucking device’ holds the ends of the wefts in place at the edge of the cloth to form the selvedge.

To reduce friction, the loom needs smooth, uniform, and appropriately sized yarn. This advanced machine operates at a lower noise in comparison with shuttle looms. Projectile looms are exclusively used to produce technical fabrics for coating.

Warp yarns are treated with sizing or lubricating compounds to minimise problems associated with abrasion in weaving. The yarn may be treated with a sizing material that is starch-based or synthetic, such as polyvinyl alcohol, or a water-soluble silicone emulsion can be used as a fabric softener in synthetic yarns to improve wrinkle resistance and as processing aids for lubrication during weaving. The sized yarns are then wound on a final warp beam and are ready for the loom [5].

It is imperative to completely remove all sorts of sizing or lubricating materials before coating because the presence of minute amounts of these materials affects rubber-to-fabric adhesion. Lint is a problem resulting from yarn abrasion (particularly of cotton fabric) during weaving. This may create complications while coating, particularly for thin proofing fabric. The presence of lint on the fabric surface also affects the quality of the fabric. Vacuum heads attached to flexible tubing move through weaving looms to remove these lints [11].

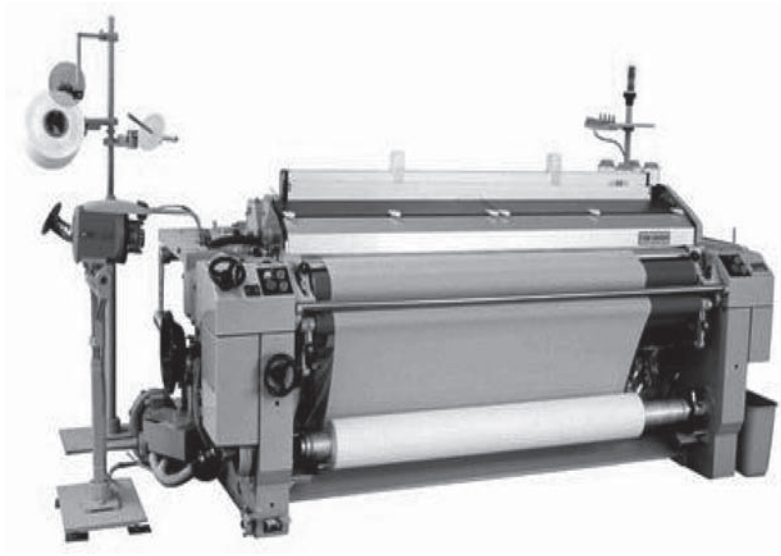


Figure 4.12 Modern water-jet loom

#### ***4.14.5 Types of Weave Patterns***

The basic weave patterns described next are commonly used for the application of elastomeric coatings to make various types of proofing.

##### ***4.14.5.1 Plain Weave***

Plain weave is the simplest of the three basic weaves. It can be formed by yarns at right angles passing alternately over and under each other. Each warp yarn interlaces with each filling yarn to form the maximum number of interlacings. Plain weave requires only a two-harness loom and is the least expensive weave to produce. It is described as 1/1 weave. This is read as 'one harness up and one harness down' or as 'one up, one down', which describes the position of the harness when forming the shed.

There are many interlacings per square inch, so plain weave fabrics tend to wrinkle easily and be less absorbent than other weaves, but ravelling may solve the wrinkling problem. However, yarn type and finishes are significant factors in ravelling. A wrinkle-free texture is necessary for flawless rubber coatings.

#### **4.14.5.2 Twill Weave**

Twill weave is a type of fabric woven with a pattern of diagonal parallel ribs. In a twill weave, each weft yarn floats across two or more warp yarns during interweaving by one to the right or left, forming a characteristic diagonal pattern. A 'float' is the portion of a yarn that crosses over two or more yarns from the opposite direction.

The fewer interlacings in twill allow the yarns to move more freely, and they are therefore softer and more pliable. Twills also recover better from wrinkles than plain weave fabrics. If there are fewer interlacings, yarns can be packed closer together to produce high-count fabrics. In twills and higher counts, the fabric is more durable and resistant to water and air. Polymer-coated twills exhibit better resistance to water and air.

#### **4.14.5.3 Satin Weave**

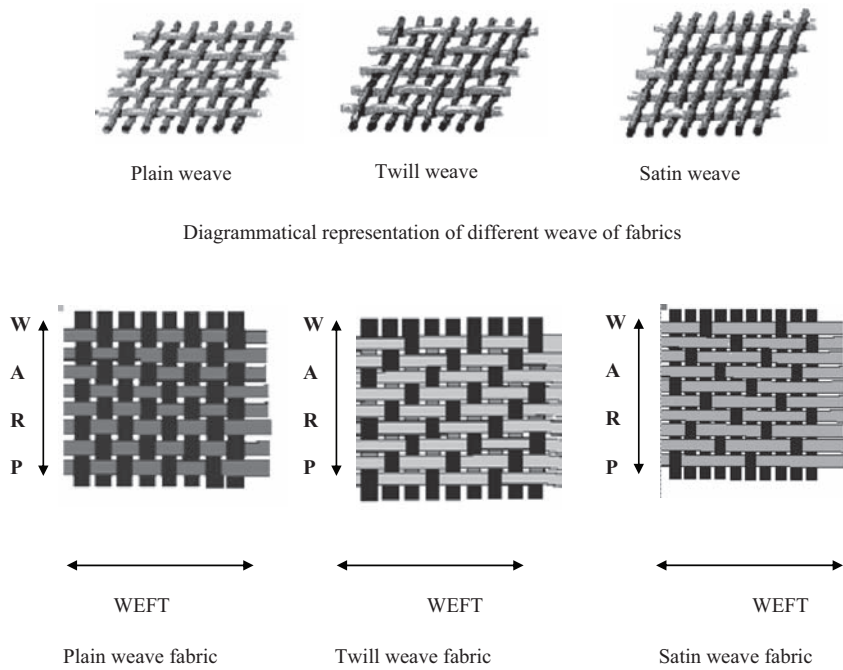
Satin weave is a weave pattern in which each warp or filling yarn floats across four or more warp yarns during interlacings by two to the right or to the left. Satin weave fabrics are the third basic weave that can be made on a simple loom. However, this weave requires at least five harnesses to achieve the interweaving pattern.

To undertake this pattern of weave, each warp yarn floats over four filling yarns and interlaces with the fifth filling yarn. This is succeeded by interlacings by two to the right or the left or each filling yarn floats over four warps, and interlacings with the fifth warp with progression of interweaving by two to the right or left.

Satin weave can be differentiated by its lustrous appearance. Satin depicts the way the threads are combined, and the yarn used may be silk or polyester (among others) to give different fabrics.

Satin-weave fabrics are lustrous because of the long floats on the surface. A high count provides strength, durability, body, and firmness, and important properties can be exploited for coated products (e.g., wind-repellence).

Satin fabrics are usually made of bright filament yarns with very low twist. Satin is almost always warp-faced: warp floats cover the surface. Because of the bright fibres, low twist, and long floats, satin is very lustrous [24]. All of these weave patterns are shown in **Figure 4.13**.



**Figure 4.13** Structure and weave pattern of textiles

**4.14.6 Knitting**

Knitting is a technique of weaving for the production of a two-dimensional fabric from a one-dimensional yarn or thread. Knitted fabrics are prepared from a single yarn or a set of yarns. During the construction of the cloth, a knitting machine forms the yarn and links it to another by means of needles. Knitted fabrics are made from a single yarn or a set of yarns. Circular knitting, which is done on circular or double-pointed needles, produces a seamless tube structure of knitted fabric. Different yarns

and knitting needles may be used to achieve different end-products by giving the final piece a different weight, texture, or colour.

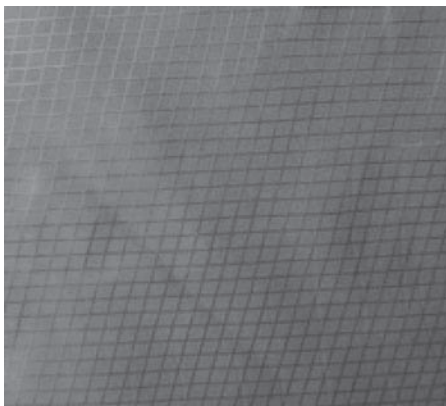
The finished fabric consists of crosswise loops. This looped structure makes knitted fabrics more stretchable than woven cloth, which gives knitting much more extendability than woven fabric. The basic knitted fabric is called a 'stocking' or 'stockinette' pattern. Depending on the yarn and knitting pattern, the knitted fabric can be stretched as much as 500%, and its elasticity allows it to follow different curvatures. Taking advantage of this particular characteristic, the knitted fabric may be coated on one side with a rubber solution and employed as a stretchable inner liner for rubber-made shoes and boots. While coating tubular fabric, it can be cut from one side to get a wide flat sheet, and spreading can be done as usual [26].

#### **4.14.7 Rip-stop Fabric**

Rip-stop fabric is a variety of woven fabric that resists tearing and ripping. Because of such special properties, the fabric has uses in special application areas. It is a lightweight woven textile with coarse, strong warp and filling spaced at intervals which prevent the propagation of tear. This category of fabric can be made by weaving two or three of the fine yarns collectively at intervals.

Nylon rip-stop is made by weaving Nylon threads throughout a base material in an interlocking pattern. Rip-stop Nylon fabric is available in lightweight types in different thicknesses and colours. This type of fabric can be made from cotton, polyester and even silk. The crosshatched threads (two series of parallel threads that intersect) makes the material tear-resistant.

Uncoated rip-stop Nylon is widely used in making parachutes and hot-air ballons where lightweight, strong and highly durable fabrics are essential. A sample swatch of rip-stop Nylon is displayed in **Figure 4.14**.



**Figure 4.14** Rip-stop Nylon fabric

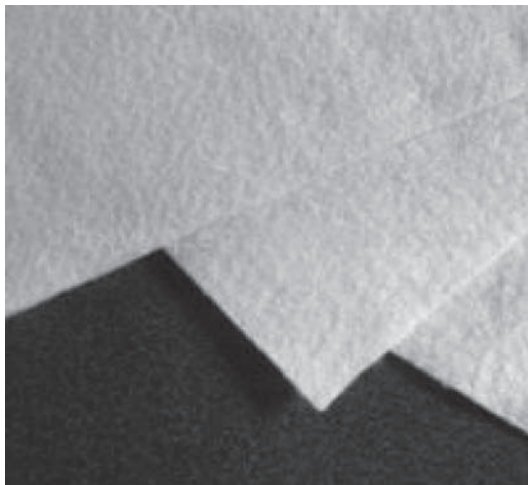
On coating with polymers (particularly if treated with a thin coating of rubber by the rubber-spreading method), it can be used for lightweight tents and sleeping bags for outdoor expeditions and for use by the military. A heavier-type material can be utilised in the making of rubber-footwear uppers for industrial and mining purposes. This type of fabric can also be used to make highly durable luggage items with rubber-coated inner liners. Rubber-coated camouflage rip-stop polyester fabric is used by the military for use in mountain terrains and woodlands. Elastomeric-coated, higher weight, rip-stop Nylon tarpaulins can be used to cover rugged surfaces as a most durable waterproof material [9].

#### **4.14.8 Non-wovens**

Non-wovens are made directly from fibres. Non-woven textiles are not woven or knitted, so there is no requirement to make yarn from the fibres. The basic fibres are laid into a web and subsequently bonded. As a result, the distances between fibres are several-times larger than the diameter of the fibres. Fabrics are made using long fibres which are bonded together by mechanical, thermal, or chemical treatment. Non-woven fabric is manufactured by putting small fibres together in a sheet and then binding them with an adhesive or by interlocking them with serrated needles such that the inter-fibre friction results in a strong fabric.

Non-wovens are low strength fabric and cannot be stretched. The properties are controlled by the selection of the geometrical arrangements of the fibres in the web. To obtain strength and durability of non-wovens, filaments and strong staple fibres

are utilised. Non-wovens can be made from synthetic fibres such as polypropylene and polyesters. Rayon and cotton fibres are used if high absorbency is necessary [27]. Polyester non-woven fabric samples for rubber-solution coatings are displayed in **Figure 4.15**.



**Figure 4.15** Polyester non-woven fabric

Non-woven fabrics provide specific performance and functional properties upon coating with specially formulated fire-retardant rubber compositions. They can be coated in a rubber-spreading machine in a solution system on one side. This type of coated non-woven polyester fabric is used for making inner linings for personal protective garments for military personnel engaged in chemical warfare. This unique property of the fabric along with application of a special type of coating can absorb lethal gases and protect the wearer. On coating with an appropriate composition of elastomers, non-woven technical geotextiles are widely used in civil applications, road construction, and soil erosion control.

## **4.15 Preparation of Textiles for Coating**

### **4.15.1 Sizing**

Sizing is added to yarns and fabrics to restrain the body of the fabric. This may provide stiffness and weight, and can improve resistance to abrasion. Application for sizing materials involves dipping the fabric in a mixture of waxes, softeners, oils, and glycerine; starch is also used exclusively. This successively controls the body during the weaving and finishing of the textiles. It is most common in cotton or cotton-blended fabrics. On Rayons, sometimes clear gelatin is applied to improve the natural sheen of the fibres. The process of sizing is temporary, and water-soluble sizing materials must be removed before the application of polymeric coatings on the fabric. Permanent sizing can be finished using resin-based materials, and upon heat-setting.

At fabric preparation before an elastomeric coating is applied, sizing materials must be completely removed from the fabric to ensure better adherence of the polymeric coating with the textile surface. Synthetic textiles are usually supplied in a ready-to-use condition for the coating industry.

### **4.15.2 Desizing**

Desizing of the fabric is necessary so that dyeing, finishing, and coatings are not affected. Depending on the sizing agents used and the fibre content of the fabric, different physical, biological or chemical processes of desizing textiles are followed. For cotton textiles and their blends used for rubber coating, physical desizing by agitation is common practice. To destroy starch (a common sizing agent), use of an amylase wash can give very good results.

Fabrics supplied from the textile loom to the coating industry to make different kinds of rubber-coated products (e.g., inflatable pillows, airbeds and rainwear), where mostly cotton fabrics are used, are often in a grey/unfinished condition. Hence, it is important to completely remove sizing residue from the fabric to prepare it for dyeing and subsequent coating.

In-house captive textile processing and dyeing units may be necessary for textile elastomer-coating factories if large amounts of textiles are consumed for coating purposes.



#### **4.15.3 Scouring**

Scouring is a procedure for removing foreign matter present in fabric before dyeing and/or rubber coating. While processing the fabric, it may be treated with processing oils (silicone emulsion is common in weaving synthetic textiles), starch and waxes for cotton, and gelatin for Rayons. During scouring, the use of detergents and alkali solutions helps to remove foreign matter.

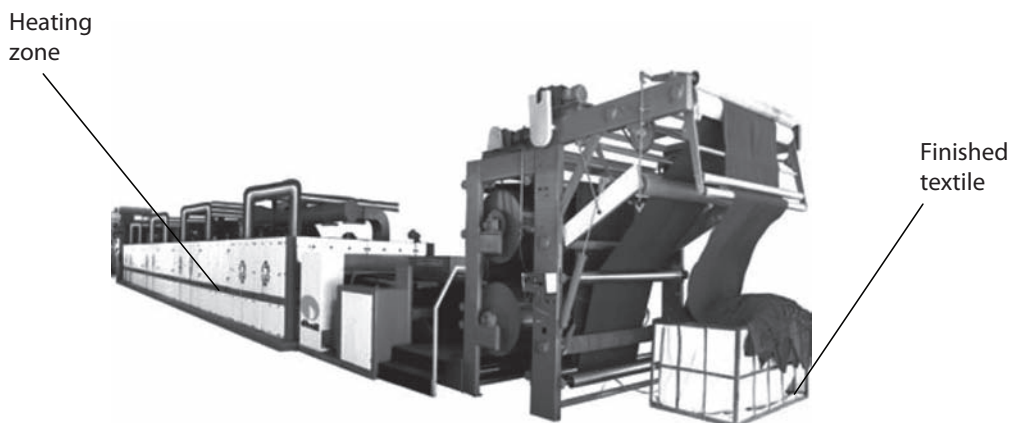
#### **4.15.4 Shrinkage Control of the Fabric**

The percentage reduction of the original dimension (in length and width) is a serious problem with textiles for the coating industry. This problem is predominant after coating, while fabricating a product from coated textiles or during service. A fabric should be made stable to retain its original shape and size before coating to facilitate building a defect-free product. Thus, maintaining the correct dimensions of the completed item (particularly for the inflated items made from it) is extremely important.

#### **4.15.5 Heat Setting**

Synthetic or thermoplastic fabrics can be heat-set at a temperature above their glass transition temperature, but it must be lower than the melting point of the fibre, and be subsequently cooled. The yarns or woven fabric made from heat-sensitive fibres stabilise upon heat-setting. This transition temperature may vary according to the type of fibre. In this method of heat-setting, the fabric is passed through the textile processing equipment (e.g., tenter) under a specified temperature. The temperature and travel time of the fabric through the tenter frame must be carefully controlled according to fibre content. During heat-setting, fibre molecules can have free movement at higher temperatures and this phenomenon relieves stress within the fibre. To maintain this molecular structure of the fibres during treatment, the fabric must be kept under a specified tension until it is cool.

This treatment can set the twist of the yarn as well as providing resistance to wrinkle and crimp weave. If the heat-setting process is done correctly, shrinkage and unusual wrinkles of synthetic fabric can be eliminated. Hence, after coating and subsequent vulcanisation, the coated material used to fabricate large inflatable equipment should be defect-free [6].



**Figure 4.16** Fabric tentering machine. Reproduced with permission from Dhall Enterprises & Engineering Limited, Ahmedabad, India

For the process of textile finishing, ‘tentering’ is an important operation to maintain the uniformity of the width while the fabric is drying. It therefore improves the quality of the finished fabric ready for coating. Using the textile tenter frame, two sides of the fabric are held by a series of clips or pins at the selvedge, and the fabric stretched to its full specified width. Lengthwise and crosswise tension is applied, and the shrinkage, bow and skew of the finished fabric controlled. The fabric can be passed through the tenter frame repeatedly for obtaining the correct width (which is of commercial importance to the elastomer-coating industry). A fabric-tentering machine and its operation is detailed in **Figure 4.16**.

#### **4.15.6 Mercerisation**

Mercerisation is a treatment administered to cotton fabric in which the strength of flat, twisted, ribbon-like cotton fibre is increased by ~20%. Usually, sodium hydroxide is used for this treatment, which improves the lustre, strength and dye pick-up of cotton fabric. If undertaken at low concentration, this treatment can also impart a silk-like appearance to cotton textiles. Mercerisation may be necessary as a step in the preparation of a good dyeing process of cotton fabric.

Dyed fabric in different colour shades is a requirement for elastomeric-coated textiles for making personal protective clothing (e.g., rainwear, wind cheaters) and inflatable items (e.g., air pillows, airbeds, water beds).

## **4.16 Dyeing**

Different finishing processes enhance the visual appearance of the fabric. In dyeing, different colours are added to the fabrics (which may be a requirement to make a rubber-coated fabric). Dyeing makes the product more attractive if it is used for making garments such as rainwear and jackets. Proofed fabric used in making uniform garments and many other applications of speciality-coated fabrics require specific colour-dyed fabric. Sometimes, a printed design is used to enhance the aesthetic appearance of the coated garments and many other rubber-coated products. To select the appropriate dye for the fabric, it is important to know the features of the dye (which have affinity for natural or synthetic fibres).

There are various methods for dyeing natural and synthetic fabrics; the commercially important methods are discussed below. Selection of the dyeing technique is dependent upon the weight of the fabric, type of fibre, nature of dye, and the extent of penetration of the dyed fabric.

Defect-free, brightly coloured dyeing of synthetic fabric is a demanding factor in making specific rubberised items for military use.

### **4.16.1 Sulfur Dyes**

Sulfur dyes can be used to dye cotton fabric used for rubber coating to produce cotton rainwear, air pillows, airbeds and waterbeds. These dyes have fastness to washing and fastness to light. These dyes are insoluble in water, but can be made soluble in water with the aid of caustic soda and sodium sulfide (soluble grades are also available). The dyeing process requires high temperatures, and a large quantity of salt is added to drive the colour into the fabric.

During dyeing the fabric is immersed in the dyebath and rinsing is done. On exposure to air, the fabric is oxidised to the desired shade (this can also be done chemically by using potassium bichromate and acetic acid). Strict control of the oxidising process is necessary because premature oxidation may retard dye penetration. On oxidation, sulfur is converted to sulfuric acid. This may affect the fabric, so it should be thoroughly washed to completely remove the excess dye and chemicals.

When compared to other dyes, sulfur dyes offer better penetration because of the high temperature of dyeing and the alkalinity of the dye bath. Sulfur dyes can give an excellent 'khaki' (drab) shade, and the shades of navy blue, brown and black to the cotton fabric used in rubber coatings for making various air-proof, inflatable and waterproof items.

#### **4.16.2 Vat Dyes**

Vat dyes are the fastest dyes. They are suitable for dyeing cotton and Rayon fabrics, and can also be applied to Nylon, polyester and acrylics by using a mordant (metal salt to bond with fibre). Vat dyes are resistant to alkalis, acids, light and oxidation.

Using a strong reducing agent such as hydrosulfite dissolved in an alkali such as sodium hydroxide make this insoluble pigment soluble. In the vat dyeing process, the fabric is immersed in the solution. The next step is to expose it in air or immerse it in an oxidising bath, which restores the dye as a part of the fibre to its insoluble form.

#### **4.16.3 Reactive Dyes**

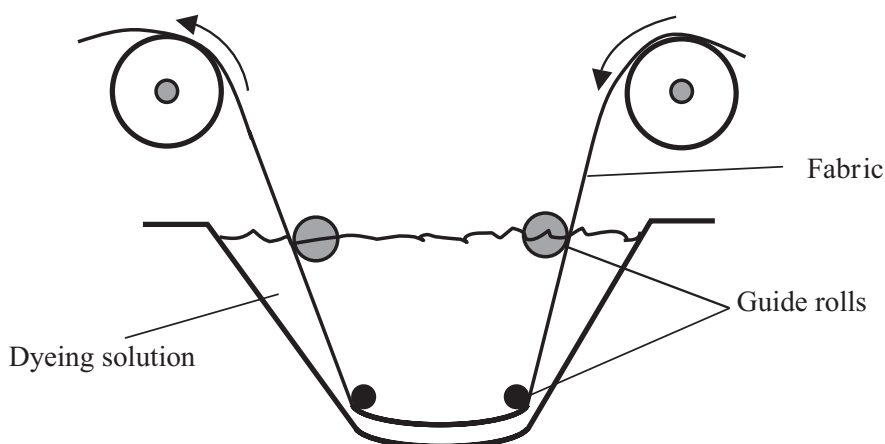
There are several varieties of reactive dyes that are commercially available. These dyes react with the molecules of the fibres to form a chemical compound. Reactive dyes are suitable to dye cotton, Rayon, silk, and Nylon. Their blends impart the fabric fastness to washing and can exhibit excellent shades.

In a one-step method of ‘pad and dry’, the dyes may be applied from an alkaline solution. Alternatively, they can be applied from a neutral solution and then alkalisied in a separate run. It is necessary to use heat to develop the shade. Soap washing after dyeing is essential to remove unfixed dye.

#### **4.16.4 Jig Dyeing**

In the jig dyeing method, the fabric is rolled up on rollers above the bath as dye under uniform tension is passed through it. Uneven tension may cause variation in the resultant shade on the fabric surfaces. Knitted fabric which cannot be stretched cannot be dyed using this process [6, 8].

This method of dyeing is more economical than other systems of dyeing cotton. Rayon, and even Nylon can be jig-dyed. In this method, a large quantity of fabric can be run for dyeing. A schematic diagram of jig dyeing equipment is illustrated in Figure 4.17.



**Figure 4.17** Jig-dyeing machine (schematic)

#### **4.16.5 Pad Dyeing**

Pad dyeing involves passing the fabric through the dye contained in a trough. The wet fabric is passed through two heavy rollers, which squeeze out the excess material and force the dye into the fabric. To set the dye, the material is run through a pad into a steam-heated chamber. It is washed, rinsed and dried in a dryer.

#### **4.16.6 Jet Dyeing**

Jet dyeing is a fast and thorough method of dyeing in which the jets of dye solution are forced through the fabric placed in a heated tube or column at 2070 kPa per jet. The cloth is moved along the tube at 200-800 m/min and the dye is continuously recirculated. This process is useful for synthetic fabrics such as polyester. The advantage of this technique is avoidance of crease and rope marks on the dyed fabric. Wrinkling of the fabric can also be avoided because of its high speed through the machine.

### **4.17 Bleaching**

The bleaching method is followed if the cloth is to be finished in a white colour. A large tank called a 'kier' is used for bleaching treatment for some fabrics (including

cotton). Bleaching can be done at the yarn stage or to the woven fabric. Depending upon the type of textile, chemical for bleaching is selected.

The kier is a big steel vessel in which the fabrics are boiled for 12 hours under pressure in an alkaline solution of 3% caustic soda solution, soap, and sodium silicate. After boiling, the materials are washed with cold water, removed from the kier, washed, dried and finished.

To obtain a white lustre of cotton fabric, the fabric can be bleached by the peroxide method. However, there is limitation of bleaching because it weakens the strength of the fibre. There is a substantial demand for white textile fabrics in the rubber-coating industry for use in domestic applications such as rainwear for civil uses, aprons and bedspreads for hospitals, and airbeds.

#### **4.18 Calendering**

The mechanical operation of finishing a fabric after desizing or dyeing (particularly cotton) fabric is done using a series of rollers. A fabric calendering machine is constructed with multiple rollers made of hard metal. The fabric is covered on a metal roll (or roll made of solid paper). The main purpose of calendering the basic fabric before elastomeric coating is to obtain a smooth surface similar to a good iron finish without creases and wrinkles.

During this process, the machine rollers are rotated at a specified speed, and the metal roll heated. Before calendering, the fabric should be moist or sprayed with water, then the fabric passes through the rolls which exert pressure, resulting in a wrinkle-free, smooth surface finish. This is essential for rubber coatings using a rubber-spreading machine or processed on a rubber calender.

#### **4.19 Speciality Treatment of Raw Textiles**

The elastomeric coating can provide protection from various threats to the coated material while in use. However, it may be necessary to apply additional protective treatment on the basic fabric so that the concoction can ensure protection (particularly in hostile environments). Such treatment to basic fabrics (e.g., for water repellency) may be necessary for application on the non-coated surface to one-sided rubber-coated fabric (single texture) converted for making raingear. This treatment prevents water absorption by the uncoated textile surface [9].

Natural fibres are likely to be damaged by fungus and insects. This can be prevented with rot-proofing and antimicrobial treatment to the basic fabric supplied by the textile mill to the coating industry. Similarly, a flame-retardant finish on the basic textile may be necessary for fire-related applications. Some very specific treatment may be demanded by the user such as a light-stabilising finish of the basic fabric.

#### **4.19.1 Flame-retardant Basic Fabrics**

Besides coating the fabric with a flame-retardant elastomeric base, the basic fabric can be made flame-resistant using inherently flame-resistant fibres or by applying flame-retardant treatment to the fabric before supplying for coating. The LOI of different fibres is shown in **Figure 4.18** and the burning characteristics of different fibres detailed in **Table 4.3**.

Inherently flame-resistant fibres include aramid fibres, modacrylic, and vinal/vinyon matrix fibres.

Flame-retardant finishes can be applied to cotton, Rayon, Nylon, and polyester fabrics. The chemicals used for flame-retardant finishes should have the following characteristics:

- They must be durable.
- They must withstand washing.
- They must be non-toxic.
- They must be non-carcinogenic.
- They should not have unpleasant odours.

Durable finishes are specific to the type of fibre to which they are applied (usually phosphate compounds or salts, halogenated organic compounds, inorganic salts). Many flame-retardant finishes are available to the textile industry. The selection and extent of treatment provided to the basic textiles should not impair adhesion with the rubber coatings [10, 27]. The limiting oxygen index of different fibres is shown in **Figure 4.18**.

Type of fibre	Burning in flame	Odour	Type of ash	Solvent
Cotton	Burns with grey colour smoke	Burning paper	Small, smooth grey	70% Sulfuric acid at 38 °C
Rayon	Burns	Burning paper	No ash unless dulled	70% Sulfuric acid at 38 °C
Silk	Burns slowly	Burning feather	Easily crushable, brittle, puffy, black	5% Sodium hypochlorite at 20 °C
Nylon	Burns and melts	Celery like	Hard grey bead	20% Hydrochloric acid at 20 °C
Polyester	Burns and melts	Sweet odour	Hard black bead	100% Meta Cresol at 139 °C
Acrylic	Burns and melts	Chemical odour	Brittle hard black bead	100% Dimethyl formamide at 90 °C
Glass	Does not burn, glows	None	Fibre remains	Hydrofluoric acid

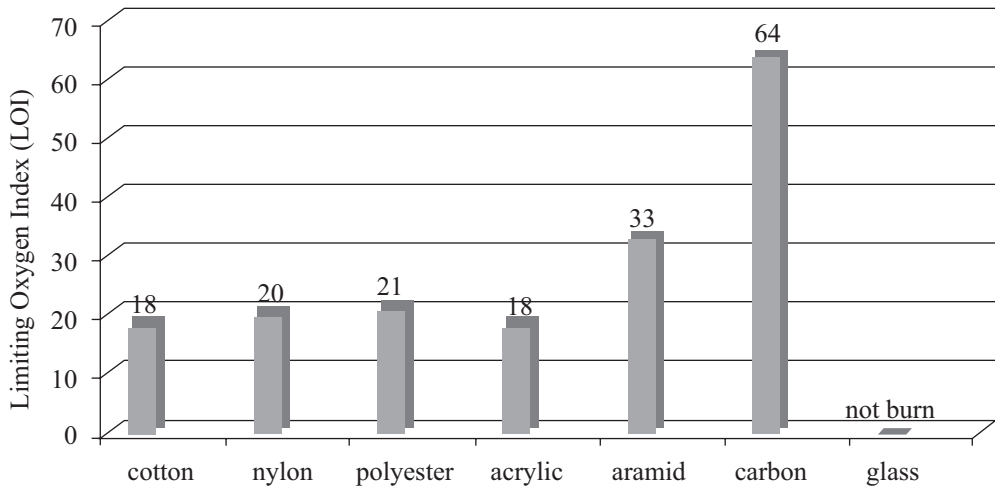


Figure 4.18 Limiting Oxygen Index of different fibres



#### **4.19.2 Antimicrobial Treatment to Basic Fabrics**

Antimicrobial treatment prevents the growth of bacteria which may cause decay and damage to the fabric during long storage before coating or during service (particularly if the coated fabric is used outdoors or comes into contact with soil and humid environments). Upon bacterial attack, the textiles also cause a bad odour due to the growth of germicides. This problem may also be found after coating (particularly in natural rubber-coated fabrics).

Antimicrobial treatment of fabrics is antibacterial, bacteriostatic and germicidal. It also provides anti-odour finishes to the fabric used for coatings which come into contact with the skin (e.g., protective garments, rubber footwear, rubberised hospital sheeting) or even in luggage items made from rubber-coated textiles.

Chemicals used for this type of treatment are (i) quaternary ammonium compounds, (ii) zirconium peroxide and (iii) *N*-halamines for cotton fabrics applied as surface reactants. The active ingredients are incorporated in liquid solutions, and can be applied by padding/spraying to the textiles. These chemicals may also be added to the spinning solution of manufactured fibres.

Antimicrobial finishes can be obtained by using chemical, gas, or irradiation treatment. If chemical antimicrobial finishes are applied to Nylon fabric, they may cause yellowing and colour fading. In some cases, ethylene oxide gas treatment is applied, but the gas is hazardous. Use of irradiation sterilisation known as electron-beam sterilisation has been introduced. This treatment is cheaper, simpler, safer, and ideal for coated products used in medical/hygienic applications. This beam can penetrate thermoplastic and foil packaging, so finished products which are packed can be treated to maintain sterility.

To prevent the growth of mildew and mould on basic textiles, the chemical salicylanilide can be used on cellulosic-based fibres. This chemical is available under the trade names Shirlan and Shirlan NA. Rubber-coated textile products used outdoors for longer periods may require rot-proof finishes: microbes in soil secrete enzymes that can disintegrate fabric.

Hence, cellulosic fibres are most susceptible to rotting. Fungicides such as *N*-methylol and glyoxal can inhibit rot-resistance properties on cotton canvases coated for tarpaulins, tentages, groundsheets, and other coated products used in outdoor applications. Moulds and mildew may grow on thermoplastic fibres, but cannot damage the fabric.

To prevent the growth of mould or mildew in the storage of basic textiles before coating, preventative measures can be taken by storing textiles in clean and dry environments. Appropriate electric lighting and an airy atmosphere may also prevent

this problem. Installation of dehumidifiers in dark and humid storage environments can prevent the growth of fungus/microbial agents on fabric which are stored in the factory [4].

#### **4.19.3 Water-repellent Treatment**

A fabric treated for water repellency can provide resistance to wetting. Water may penetrate the fabric when the striking force of water is high. If a fabric is coated with an elastomer which forms a protective film, it will not become wet if exposed to water for long periods, and will not allow water to penetrate the fabric if the striking force of water is increased.

The water repellency of a fabric is dependent upon the surface tension and penetrability of the fabric. This can be achieved by a combination of the structure and finish of the fabric. The chemical compounds used to treat the uncoated basic fabric to make it water-repellent are (i) fluorocarbons, (ii) wax emulsions, (iii) metallic soaps and (iv) surface-active agents. These chemicals may be used as water-based solutions on fabrics of high warp count with small, regular yarns.

The method of application of water-repellent finishes on uncoated or one side rubber-coated fabrics is by padding. The fabric is passed through the solution under a guide roll, and between two padding rolls. Hence, the finish is distributed across the fabric width while it is passed through the padding rolls. With the pressure of the rolls, the chemicals are forced into the fibres and the excess liquid is squeezed off. The fabric is then dried by passing through a steam-heated zone. A backfilling machine can be used to apply a finish to the back of the fabric or to one side of the rubber-coated fabric.

Some of the one-sided rubber-coated fabrics (single texture) used for making fashionable coloured rainwear or snow wear involves the uncoated textile surface being on the outside and exposed to moisture. These coated textiles can be treated with water-repellent chemicals to make the gear water-resistant to provide comfort to the wearer. Using this technique may improve water- and oil-repellency if fluorocarbons are applied.

The most commonly used water-repellent chemical is silicone, which can make the fabric soft and stain-resistant. Other water-repellent finishes are available (e.g., trade names Scotchguard, Teflon). These readymade chemicals can impart resistance to stains due to oil or water on the fabric surface, and are available as sprays [24, 28].

## **4.20 Fabric Inspection and Quality Assurance**

Inspection of the basic input fabrics for a coating factory is challenging because the industry uses different types of yarns, weave patterns, and various colour shades to maintain quality standards for rubber coatings and to fabricate defect-free end-products. It is evident that fabrics, mostly cotton textiles, can show some degree of imperfection. Examining precisely the overall consistency of the fabric to ensure the quality of the finished goods after coating is imperative. It may be for the making of personal protective gear for domestic users or for critically designed engineered devices for life-saving equipment for the defence forces. This may differ from company to company producing a particular type of coated items.

Quality inspection of the basic fabric, whether it is natural or synthetic, before sending the fabrics to the Coating Department for further processing is very important. In general, all types of fabric inspection may be conducted by slowly moving the fabric on an inspection table fitted with a light screen. The fabric from the let-off roll fitted on a frame on the rear end of the table is pulled by hand over a light screen and wound at the front. A glass screen is fitted on top of a box made of ply wood or sheet metal installed with a light source on the bottom of the box. The light screen box is built-in at the front of a long table.

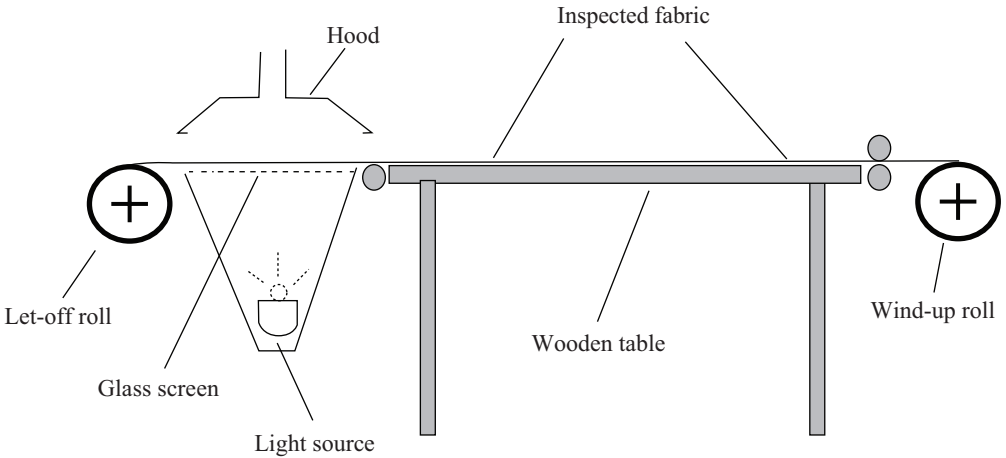
This system of fabric inspection is to visually identify the quality of fabric received from the fabric supplier. The flaws detected during visual inspection are within the acceptable limit and if the defect is repairable, the material is accepted for coating. Broken yarns, snagged yarns or missing threads are marked, and these portions can be cut after rubber coating to make short-length pieces, if this is acceptable for the fabricators of the coated material or the end user [6].

The fabric is also checked for being skewed, biased, or having a bowed defect because these are carefully inspected when the coated fabric is utilised for the fabrication of inflated engineering items. A fabric inspection table is displayed in **Figure 4.19**.

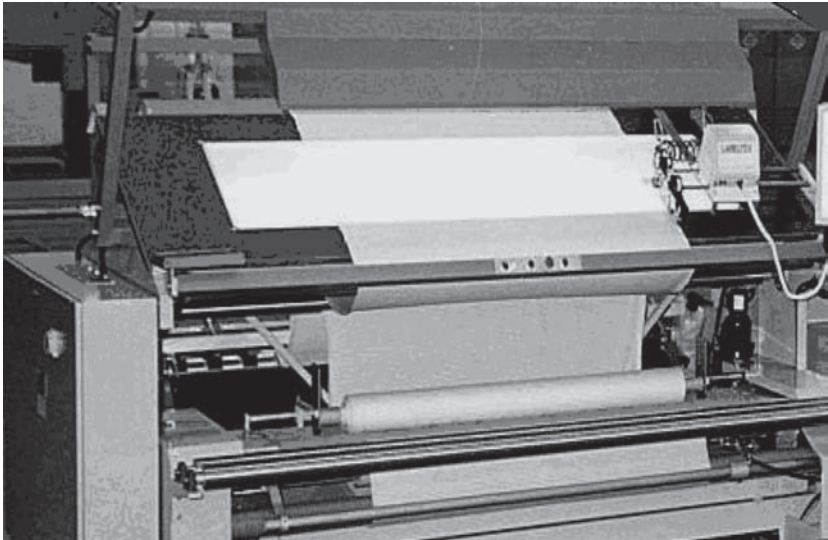
Defect recognition of woven fabrics is not limited to slubs, holes, missing yarns, or the variation of yarns; dyeing or printing defects (particularly for the coloured and different printed fabrics converted in making garments after elastomeric coatings) are also examined. Dyed and printed textiles used for fabricating rainwear for children and women, wind cheaters, backpacks, and for making coloured luggage items, need to be carefully inspected visually on the inspection machine. A fabric inspection machine is shown in **Figure 4.20**.

In this machine, visual defects can be inspected in a roll of fabric fixed and slowly unwrapped by pulling from the other side by a motor. The fabric is displayed on a

screen under sufficient lighting at a controlled speed of passing the material to detect the defect. The machine should run at a slow speed to effectively locate the flaws visually.



**Figure 4.19** Fabric inspection table (schematic)



**Figure 4.20** Fabric inspection machine with a measuring device

The usual dyeing and printing defects are dye spots, streak marks, colour smears, machine stop marks or shading. A measuring device is fitted to the machine to measure and record the quantity of fabric inspected and to determine the length of the fabric supplied by the fabric manufacturer in a roll.

Inspection can be done by turning off the light to see how a flaw can affect the appearance, which may be detected after the coating. This type of inspection is imperative for items produced for military use, particularly if they are life-saving devices made out of coated fabric. The observed defect can be marked with coloured chalk or coloured tape so that the defective part can be avoided while designing and cutting for fabrication after coating.

For the quality assurance of the finished product after coating, swatches may be cut from the basic fabric to examine physical characteristics such as (i) weight per square metre, (ii) number of threads per inch warp and weft directions, and (iii) break and tear strength. For coloured and printed fabric, the tests conducted are (i) colour fastness in washing and (ii) colour fastness under UV light.

Fabrics are transferred to the coating plant in large quantities every day, so appropriate inspection and quality checking must be established to save labour and time. Electronic sensors and computers are used to evaluate the quality of fabric [18].

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# 5 Basic Features of the Manufacturing Technology of Polymer-Coated Textiles and Fabrics

**Bireswar Banerjee**

## 5.1 Introduction

Over the years, the technological development of rubber and textiles has been sustained by making improved rubber textile composites that can be used under diverse and aggressive environments. Examples of such environments include very high or low temperatures, in outer space, or under the sea.

The name ‘rubber’ was given by the English chemist, Joseph Priestly in 1770 when he observed that a small piece of caoutchouc could be used to erase a pencil mark. Since 1775 until today, this rubber has been called ‘India rubber’ in English speaking countries [1].

Textile coating technology was first used in the 1820s when Charles Macintosh in the UK, using a rubber solution prepared in solvent, conducted the first fabric coating and applied the solution to a textile fabric to make the fabric waterproof.

In 1823, Charles Macintosh started a rubber-coating factory in Glasgow, UK. He later moved to Manchester (the facility is still operational). Handmade hoses on mandrels using plies of fabric as reinforcement were made in 1825.

Thomas Hancock discovered rubber mixing by using a simple machine in 1830 [1].

To control the problem of softness and stickiness of the original rubber due to seasonal changes in temperature, the rubber was positioned in-between two textile fabrics. This generated the idea of making a ‘double-texture (DT)’ coated, waterproof fabric or ‘mackintosh’. The problem of softening during environmental changes in temperature was surmounted by the invention of vulcanisation.

The first rubber processing machinery was developed in 1835, when Edwin Chaffee in the USA invented the first calendering equipment for coating cloth. Hancock also invented the rubber-spreading machine in 1837 for coating rubber on fabric in solution



form. Since then, rubber calender machines have become more accurate and faster to produce more versatile, defect free rubber-coated textile products [2]. Hancock and Macintosh collaborated and started producing air pillows and airbeds, which were used by King George IV when he was on his deathbed in 1830.

A revolutionary discovery in the history of rubber processing was made by Charles Goodyear when he conducted vulcanisation of rubber in 1838 in the USA. Vulcanisation converts rubber to a durable and flexible material from its original clay-like consistency. Following his work, several interested parties started experimentation on rubber-coated fabrics. The method of 'cold curing' for proofing and dipping rubber articles with sulfur monochloride was invented by Alexander Parkes in 1840 [3].

Hot vulcanisation of rubber with sulfur was invented by Thomas Hancock in the UK in 1843. To speed-up the vulcanisation process, the organic accelerator was invented by George Oenslager in 1906 [4].

After the invention of rubber accelerators to boost the vulcanisation process, thiuram disulfide was introduced in 1912, this made it possible to cure rubber without the use of elemental sulfur [1]. The rubber accelerator mercaptobenzthiazole (MBT) was first used in 1921. At the same time, it became known that zinc oxide improved the action of organic accelerators [3].

Cord fabric was introduced to reinforce tyres in place of woven textiles in 1914. The introduction of the Banbury mill to the industry was made in 1920 to meet the requirement of bulk production.

Several methods were being used for coating textiles with thermoplastics. This led to the technique of extrusion coating being introduced in late 1940s in the USA.

## **5.2 Process of Coating Textiles**

The manufacturing technology of coating textiles and fabrics is to apply a layer of rubber elastomer (or another polymeric material) directly to one surface or to both surfaces of the substrate, irrespective of whether it is woven or non-woven. The primary requirement is that the polymeric coating must adhere to the textile surface. To apply a thicker coating, it may be necessary to repeat the successive layers of coating if a spreading system of rubber coating is undertaken. Again, the adhesion between the layers should be correct. Also, the final coating must be aesthetically appropriate as well as enhancing the technical requirements of the coated material.

Polymeric coatings on textiles improve and extend the range of functional properties

of the finished product. Hence, this technology is growing rapidly, and the application of technical textiles has become more diverse.

Coating on technical textiles has become increasingly important and popular. This has led to fabrication of articles for domestic wear, sportswear, personal-protection articles, as well as articles for engineering, military, and healthcare applications.

For thermoplastic polymers, coating on textiles using modern machinery and processing techniques gives good results and offers specific finished products.

Depending upon the product requirements, the weight of a coated textile may be 10-20 g/m<sup>2</sup> to >600 g/m<sup>2</sup> [5].

On selection of the correct elastomer and appropriately formulated rubber compounds, as well as providing a coating at the desired thickness and weight to the substrate, a technical textile can offer resistance to water, air, gas, oil or fire. These are ultimately used in the fabrication of different industrial equipment.

Pretreatment of textiles before coating, such as heat-stabilisation to maintain fabric dimension (particularly for synthetic fabrics), is very important. Treatment with a bonding adhesive can be prepared in-house, adhesive dips [resorcinol-formaldehyde (RF), vinyl-pyridine (VP) latex dip] or using a proprietary bonding agent before coating is necessary for synthetic textiles to get the desired adhesion properties to the finished material.

Elastomeric coating can be applied to cords, knitted, non-woven or woven fabrics for many industrial and technical uses. The machinery and equipment, as well as the methods for applying rubber coatings, must be appropriately designed to avoid excessive stretch or distortion of the fabric used, and to eliminate processing problems during coating operations. The lighter the weight of fabric selected for coating, the more control is necessary during the process.

Two main processes are usually used for applying rubber compounds on natural and synthetic textiles:

- A wet system consisting of a solution or solvent dispersion by dipping and spreading.
- A dry system using calendering.

The purpose of coating the woven textile, non-woven fabric or cord is to provide specific properties to the final coated products, and to make the textile one or more of (a) waterproof, (b) air-proof, (c) gas-proof, and (d) chemical-proof.

Application of an elastomer coating to the textile substrate facilitates the building up of a fabricated item in the unvulcanised condition, and the built-up product can then be vulcanised.

Rubber-coated fabrics are used in the manufacture of waterproof items, inflatable devices, agricultural and industrial hoses, conveyor/flat beltings, tyres, tarpaulins and tents. They are also used in several applications for domestic, industrial and military requirements [6].

Textiles and cords not only contribute reinforcement to the end-product but also offer other important properties. Some of the products made from non-woven fabrics coated with rubber compounding ingredients are used in gas-absorbent personal protective equipment for the military.

If needed in high shock-absorbent conditions, some speciality fabrics such as aramid fabric, glass fabric, carbon fibres and materials such as steel cord/metallic mesh on rubber coatings are used as reinforcing constituents if very high strength, high flex and heat resistance of the end-product is required.

### **5.3 Rubber Textile Adhesion**

In achieving adhesion between the textile substrate and elastomer matrix, the following methods are used by fabric coating industries:

- Adhesion by mechanical methods.
- Treatment of fabric by dipping the textile with aqueous resorcinol-formaldehyde latex (RFL).
- Treatment with rubber solution and isocyanate.
- Using a proprietary bonding solution with a rubber solution or dipping into the rubber solution.
- Direct addition of dry bonding agents to the rubber composition.

Natural fibres such as cotton have staple ends and provide mechanical anchoring with the protruding ends, so they may not require pretreatment for bonding in producing items for general use. Special adhesion treatment is necessary to improve the bondability of the rubber layer with the substrates for synthetic textiles, synthetic cords, and steel cords.

### **5.3.1 Resorcinol-formaldehyde Latex Dipping**

One method for obtaining good adhesion between a rubber matrix and a synthetic filament yarn substrate such as Rayon, Nylon or polyester is to dip the cord/fabric in RFL suspension. This is an aqueous system containing a resorcinol-formaldehyde resin. It aids adhesion to the textile material, and the latex helps to promote adhesion to the rubber cover and the textile.

This adhesive system is employed for the pretreatment of Rayon, Nylon, polyester and other synthetic textiles and cords. Rayon and Nylon have high surface polarities, so therefore strong physical and chemical bonding takes place between the RF resin and the cord/textile surface.

The RFL aqueous dispersions are made-up of a terpolymer of styrene, butadiene and VP. The condition of resin formation and pH of the resin solution, choice of latex, and the ratio of latex/resin are the important factors for improved adhesion properties with the rubber coating and substrate [7].

The resin can be prepared by condensation of formaldehyde and resorcinol or by the addition of formaldehyde to a commercially available preformed RF resin (Penacolite R2200, Indspec Chemical). Resin condensation occurs in the presence of ammonia or sodium hydroxide (or a combination of both). Commercially available VP latex (Pliocord VP 106, Goodyear) with 15% VP content can be used. Pre-condensed RF resin (Vulkadur T, Bayer) available in 40% aqueous solution may be incorporated with latex and formaldehyde [8].

The type of latex used can be of natural rubber (NR) latex, styrene butadiene rubber (SBR), acrylonitrile (ACN), polychloroprene (CR), and VP, but good properties can be obtained with a mixture of latices. The selection of latex must be compatible with the elastomer used in the compound for subsequent textile coating. It is even more important if the coated compound of a CR- or nitrile-rubber based is used.

If a flame-resistant coated fabric material is required, the latex should have flame-resistant properties and these can be further enhanced by the addition of flame-resistant additives such as chlorinated paraffin/antimony trioxide.

For the treatment of Rayon, the latex components are SBR and VP lattices. The ratio is maintained at 80:20. For the treatment of Nylon, 80-100% VP latex can provide the desired adhesion.

Rubber-to-fabric adhesion is better with RFL dip cords or fabric in dynamic stresses when compared with the bonds obtained using RF resins prepared in-house. The bond strength becomes stronger and more resistant to dynamic stresses if RF treatment

comprises VP latex.

To obtain good mechanical anchorage, the major proportion of the dip should be available on the surface of the threads, and the degree of penetration should not be too high. If excessive penetration of the dip into the fibres occurs, this reduces the concentration of the dip available to the surfaces, resulting in impairment of adhesion to the surface. Excessive penetration of the dip also causes a stiff material and sticky filaments; this may increase heat build-up under dynamic stress and can affect adhesion.

Control of the viscosity of the RFL dip can maintain the depth of penetration. Another method of penetration control (particularly for cords) can be made by adjustment of the tension while it is passing through the dipping operation; increasing the tension reduces the depth of penetration.

The final adhesion strength is dependent upon the following factors:

- Structure and chemical nature of the fabric.
- Thickness of the dip.
- Design and function of the dipping plant.
- Removing excess latex under fabric tension at speed while the fabric is drawn through the bath.
- 4-8% dip should remain on the fabric compared with its original weight.

To help the drying operation after dipping, the fabric is exposed at 120-180 °C for 1-10 minutes; this also completes the condensation of the RF resin. Higher temperatures may be applied to simulate curing of the RFL-dipped material in an oven at 230 °C for 90 seconds [7]. A typical composition of a RFL system is given in **Table 5.1**.

<b>Table 5.1 General composition of the RFL system</b>	
<b>Component</b>	<b>Parts wet</b>
Water	100.0
Sodium hydroxide (10%)	7.0
Formalin (37%)	13.8
Resorcinol	9.4
VP latex (40%)	212.0

During the vulcanisation of dipped materials after coating with rubber compounds, the curing agents present in the rubber compound diffuse into the RFL dip. This helps the crosslinking of the latex polymer, which promotes adhesion between the dip and the rubber matrix. It also influences the mechanical properties of the RFL dip. A complete RFL dipping plant displayed in **Figure 5.1**.

Further development of the method of promoting adhesion between the textile and rubber in a RFL dipping system has been carried out by Mortin and colleagues in the USA. The invention is claimed to be a ‘vinyl compound plasma pretreatment procedure’ with subsequent application of RFL to the textile surface. This method encompasses a process through which free radicals of compounds comprising strong carbon–carbon bonds form a film over the textile film and then covalently bond to the resin component of the RFL. Such a method produces an extremely strong and versatile adhesive that facilitates adhesion between rubber compounds and heretofore unusable or difficult-to-use textiles. This procedure can be suitably undertaken in the manufacture of conveyor belts, rubber dams, pneumatic fenders, and floating bridges, where extremely high bond strength is imperative for enhancement of the service life of the products.



**Figure 5.1** RFL dipping plant. Reproduced with permission from Swastik Textile Engineers, Ahmedabad, India

### **5.3.2 Dry Bonding System**

In the bonding of textiles such as Rayon, Nylon, polyester, aramid and glass fibre coatings with NR-, SBR-, nitrile-butadiene rubber- (NBR)- and CR-based mixes, the dry bonding agent is added directly to the rubber compound during mixing. This is highly effective and may not involve pretreatment of the substrate.

Before the incorporation of accelerators during the mixing cycle, resorcinol and precipitated silica in the proportion of 4-6 phr with a combination of hexamethylene tetramine (HMT) coated with silica (1.5-2 phr) can be added directly to the rubber compound. To get the best adhesion, the curing system of the rubber matrix should be based on a delayed-action accelerator such as a sulfenamide accelerator or sulfur. This produces a stable highly crosslinked elastomeric network upon heating because it decomposes to produce ammonia and formaldehyde, which reacts with the resorcinol.

The direct bonding agent – modified melamine compounds such as hexamethoxymethyl melamine (HMMM) resin mixed with silica filler as a free-flowing powder – can also be incorporated directly during mixing. In certain applications, HMMM resin-based bonding agents offer improved adhesion to rubber textile composites when compared with HMT. It shows better performance after ageing in humidity and steam. This dry bonding agent is available with 50-70% resin content [7].

### **5.3.3 Chemical Bonding Method**

Active polyisocyanates, a 20% solution of triphenylmethane tri-isocyanine in methylene chloride (Desmodur RE and RF, Bayer) provide highly satisfactory bonding to a wide variety of elastomer and synthetic textiles. CR-based adhesive added with the isocyanate can be used for CR, NBR and chlorosulfonated polyethylene coatings on various synthetic textiles. These trifunctional compounds endow chemical linkages between the fabrics and rubbers.

In a chemical bonding system, use of isocyanine dissolved in ethyl acetate or methylene chloride in the correct proportion can be added to a rubber solution of low viscosity with a low dosage of accelerator and sulfur to make the mix a delayed curing system. This can be mixed by hand-stirring or by slow-speed mechanical stirring. The prepared adhesive can then be applied on synthetic textiles in a rubber-spreading machine as an adhesion coating and dried before subsequent coating in a spreading machine or in a calender to achieve good adhesion with the textile substrate.

Isocyanates are exceptionally active crosslinking agents. Hence, their pot life if added to the rubber solution for coating is very short. Care should therefore be taken

regarding their utilisation. Their sensitivity to moisture may impair effectiveness, so care should also be taken on the process of use. Isocyanates stain upon exposure to light. Hence, they can be considered only for black rubber coatings or if staining to some extent is acceptable [9].

To achieve adhesion, isocyanates can sometimes be employed in conjunction with chlorinated rubber to promote higher bond strength.

Care should be taken with regard to the storage and use of these chemicals because atmospheric moisture may affect their efficiency.

Another important use of isocyanates in rubber adhesives is the preparation of self-curing cement. This is widely used in the fabrication of rubber-coated textile articles made from cured coated material.

#### **5.3.4 Steel Cord Adhesion**

Adhesion promoters such as cobalt naphthenate (10.5%) are very effective in the bonding between rubber and zinc-coated or brass-coated steel cord, which enhance the performance and durability of the end-product. Cobalt stearate (9.5%) and cobalt boroacylate also offer very good results. Proprietary bonding agents for steel cord such as Manobond 680 C and Manobond C 22.5 are highly effective steel cord promoters for rubber-steel adhesion.

During reinforcement with brass-plated carbon steel wires using NR compounds with a sulfur curing system, a chemical interaction takes place with the brass and rubber during vulcanisation. This produces a copper sulfide adhesion layer that bonds the wire to the rubber cover. Addition of a small quantity of precipitated silica in the mixes can also promote adhesion to brass-coated steel wires [10].

The brass surface of the coated steel cord, if insulated with rubber compounds, is exposed to active sulfur molecules in the rubber compound during vulcanisation, and effective bonding is produced between the rubber compound and the steel cord [7].

Where steel wire is used as reinforcement (e.g., conveyor belts, hoses, tyres), brass plating is considered to provide adequate bonding when it is insulated by rubber. Bonding strength can vary with the brass composition and plating thickness but, if higher bond strength is necessary, use of direct bonding agents in the insulation stock can offer improved results. These bonding agents are usually cobalt soap compounds such as cobalt naphthenate or cobalt stearate.



If improving the adhesion under unaged conditions is required, use of proprietary products such as Manobond C-16 liquid (Manchem) can significantly improve adhesion. This agent has 16% cobalt content; it is a complex metal organic compound based on cobalt and boron linked through oxygen to an organic component [11].

### **5.3.5 Proprietary Bonding Agents for Textile Adhesion**

Widely used general purpose proprietary bonding agents such as Chemlok 402 (Lord Corporation) can be effectively used for bonding Nylon and polyester textiles. These bonding agents can be diluted in solvents such as xylene/toluene. They can also be used without dilution, spread on textile surfaces or be used in the dipping process. They can provide very good adhesion.

Bonding of glass textiles and other synthetic fabrics with silicone rubber coatings is achievable by the use of Chemlok 607 (Lord Corporation), a clear, colourless liquid bonding agent applicable for white and coloured coatings. Dipping or application by padding (in dilutions with methanol or ethanol) of this adhesive give improved results if both faces of the substrate are to be coated on glass textiles.

Adhesive coatings should be properly dried before application of rubber coatings. This is done by passing them over steam heated chests; coatings can also be applied in a spreading machine or in a calender machine.

## **5.4 Coating of Fabrics with Thermoplastic Polymers**

For coating thermoplastic polymers on textiles (Figure 5.2), the following methods are usually used:

- Hot-melt process
- Transfer coating
- Lamination
- Solvent-based system
- Flame lamination
- Extrusion coating

#### **5.4.1 Hot-melt Process**

The hot-melt process involves calendering the molten thermoplastic polymer, which is softened or melted by heat and which can then be directly coated on the textile using a pair of calender rollers. In another system, the molten polymer is extruded directly onto the fabric from a slotted die. A smooth coating is then obtained by contact with a polished 'chill roller'. An engraved roller can be deployed to get a desired patterned surface of the coating.

There is also a method of grinding down the hot-melt adhesive particle to a size of 60-200  $\mu\text{m}$ . It is then applied from an engraved roller heated up to 250 °C of a specific design to a heat-stable fabric. A second fabric is brought into contact while the adhesive is in molten state to produce a double-textured fabric.

#### **5.4.2 Transfer Coating**

Transfer coating is an indirect coating method. The coating material is cast and formed on a silicone-coated release paper.

The main advantage of using this technique is that a perfect film is formed before transferring it to the surface of the fabric by the application of heat. Alternatively, a tie coat of suitable adhesive can be applied on the fabric surface. A thin lightweight coating is possible on technical fabrics and the silicone-coated release paper can be reused several times [12].

#### **5.4.3 Lamination**

In the lamination process, a combined fabric consists of two or more layers. One is a textile fabric, bonded together by using an adhesive or by adhering one or more component layers. Laminated technical textiles comprise one or more textile substrates that are combined using a pre-prepared polymer film or membrane by employing adhesive or pressure and heat. A polymeric substance can be layered in a laminated fabric using an hot-melt adhesive.

#### **5.4.4 Solvent-based Adhesive System**

Solvent-based adhesive systems are used to laminate microporous membranes to textile fabrics. Polyurethane polymers can be dissolved in solvent which can be cured in the

presence of moisture. It is sprayed onto the fabric, and the fabric is pressed on the adhesive surface. Crosslinking takes place to form the bond. Because of environmental concerns, solvent-based adhesives are beginning to be replaced by hot-melt adhesives.

#### **5.4.5 Flame Lamination**

In flame lamination, polyurethane foam can be made to adhere to textile materials if polyurethane foam from a supply roller is passed over a gas flame at 950 °C, and then combined with textile materials from a second roller in the first nip of a three-roll machine. The foam laminated textile material is then passed through the second nip and the third roller used as a wind-up roller.



**Figure 5.2** Thermoplastic polymer coated fabric

#### **5.4.6 Aqueous-Based Adhesive Lamination**

In this method, aqueous-based pressure sensitive adhesive is applied using a spreading machine of the knife-over roll system to laminate two fabrics. The pressure sensitive

adhesive can be spread on a release paper and transfer coated to a textile surface. It is then combined with a second fabric by adhering the two in contact under pressure and heat. Water is removed from the laminated material and bonding takes place. Adhesives based on NR, SBR, acrylics, and polyvinyl alcohol can be used for this method of lamination.

The second process is to apply aqueous-based adhesive using hot-melt polymers by using a rotary screen-printing system. An infrared heating system is used in which water is evaporated and the polymer melted. A second layer of material is brought into contact with it to enable bonding. The adhesives may be foamed, applied in a specific pattern, and spread by a second blade after the print head.

Using this technique of coating, the coated textile can be made soft-to-handle and with breathable properties. Appropriate control must be taken if heat sensitive textiles are being processed. Adhesives of aqueous-based solutions of polymers such as polyethylene, polyesters, ethylene vinyl acetate, polyurethane, and polyamide can be utilised.

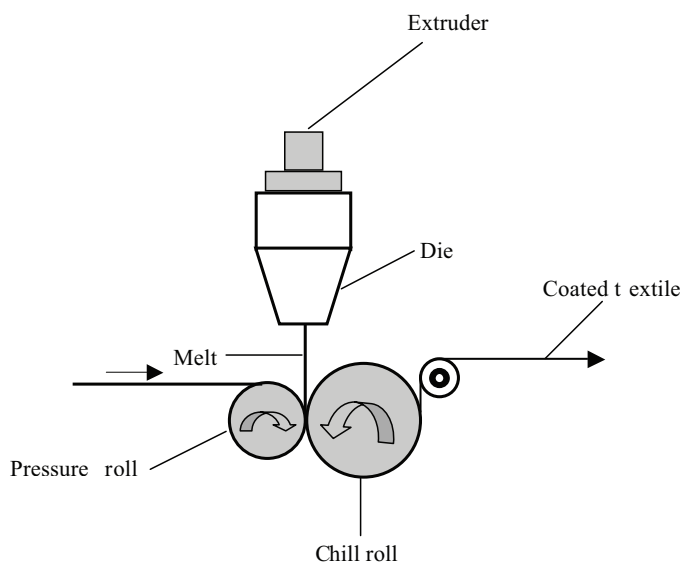
#### **5.4.7 Extrusion Coating of Thermoplastics**

Extrusion coating is a continuous process used to coat a flexible substrate such as woven textile with a thermoplastic polymer.

In a typical extrusion, in the coating machine, the substrate at a constant tension arrives into the coating nip via a series of 'idler rolls'. Hot and molten polymer is pressed into a substrate which is passing through a cooled nip roll assembly. The extrusion coating process using thermoplastic materials is illustrated in **Figure 5.3**.

Upon textile coating, the thickness of a thermoplastic  $\leq 0.5$  mm is obtainable using this method. The weight of the coated material can be 10-75 g/m<sup>2</sup>.

The machine where the melt is to spread and adhere to the substrate is called the 'coating section'. The melt enters into the nip almost tangential to the chill roll [13]. A water-cooled 'back-up roll' removes excess heat from the surface of the rubber pressure roll; the distance between the die and nip influences adhesion to the substrate. The diameter size of the extruder for thermoplastic coatings ranges from 90 mm to 150 mm. Chilled water supplied at 15-20 °C is pumped through the rolls; the water capacity is 1500 l/min.



**Figure 5.3** A typical extrusion coating machine (schematic)

## **5.5 Preparation of Rubber Compounds for Coating Fabrics**

Designing a rubber compounding recipe for the preparation of a composition to use in textile coating applications is a complex process. It contains a wide range of chemicals based on the type of rubber (natural or synthetic). Different additives are added depending upon the type of synthetic rubber and its product properties. The preferred method of coating textiles is the basis upon which the coating machinery is selected. The colour of the coatings is chosen from black, white, attractive bright colours or fluorescent, but all are dependent upon the end requirement of the coated material. It is important to ensure that the prepared rubber compound is a homogenous mixture to get the desired properties of the products.

### **5.5.1 Rubber Compounding: Preparation Methods**

The basic and primary requirement of the rubber processing industry is to prepare a compound of rubber that is suitable for processing the product to be produced. Preparation of the rubber compound involves mixing various compounding ingredients in a rubber matrix based on NR or synthetic rubber.

*(i) Weighing of the Ingredients used for Compounding*

The 'Drug Room' is an important section for the polymer processing industry. This is where the rubbers are cut into smaller pieces from bales, and where bulk fillers and fine chemicals are weighed accurately according to the pre-designed recipe from the Technical Department. An automated system of weighing is available for weighing of the chemicals.

Semi-automatic and electronic weighing scales are commonly used by the medium and small-scale processors who are the major players producing coated fabric articles. Accuracy in weighing and cleanliness are the primary criteria for the weighing section of a rubber processing factory.

Before being sent for weighing, bulk and fine chemicals require a quality check to maintain the consistency of the rubber compositions as well as to conform with product specifications.

The primary controls are:

- Viscosity of polymers.
- Mesh size of the bulk fillers (particularly white fillers).
- Melting point of fine chemicals.
- Specific gravity of the fine chemicals.
- Basic chemical testing of the fine chemicals.

*(ii) Process of Mixing Rubber Compounds*

In the dry process of mixing, the rubber is softened and the filler agglomerates breakdown into smaller aggregates and distribute uniformly in the rubber. The process is highly energy intensive and the equipment must impart a high shearing action to the materials. The resultant product should be a homogeneous mixture of chemicals, additives, fillers and base rubber.

### **5.5.2 Rubber Compounding Ingredients**

Designing a rubber compound or formulating a recipe is the 'backbone' of textile coating manufacture. The composition/mixed material is processed in different stages of the operation for coating, such as initial mixing, storing, warming, calendering, and vulcanisation. In addition, for spreading, dough has to be prepared in a dough

mixer with a solvent. All these operations must be carried out safely to obtain a quality finished product when a coating is applied on a textile substrate or on cords or steel cords.

A compound is made based on raw rubber and other ingredients (e.g., chemical peptisers, accelerators, activators, reinforcing/non-reinforcing fillers, process aids, tackifiers, anti-degradents, colours) are added where necessary [10].

#### ***5.5.2.1 Functional Classifications of Rubber Compounding Ingredients***

In general, the functional classifications of rubber compounding ingredients are incorporated in the formulation for textile coatings, as listed next:

- Rubbers: NR or synthetic rubbers (or blends of NR and synthetic rubber) are the base material used to make a compound.
- Tackifiers contribute to the formation of building tack if the coated material is fabricated in an unvulcanised condition to build-up an article, and to improve adhesion while coating on a substrate. Tackifiers include natural rosins, phenolic resins, hydrocarbon resins, and tars.
- Vulcanisation inhibitors or retarders provide scorch safety to the compounds if they are processed for coating (particularly during calendering).
- Activators to accelerators and vulcanising agents help to form crosslinks during vulcanisation. A vulcanising agent for NR and many synthetic rubbers is sulfur; widely used activators to accelerators are zinc oxide and stearic acid. In halogenated rubbers, zinc oxide functions as a vulcanising agent.
- Colourants and pigments may be inorganic or organic. For instance, white pigments such as titanium dioxide and red pigments such as iron oxide are inorganic. Organic colourants are brightly coloured pigments available in different colour ranges and shades.
- Fillers/extenders are reinforcing or non-reinforcing. The most important fillers in the reinforcing group are different grades of carbon blacks, silicas and silicates (including fumed silica, precipitated silica, aluminium or calcium silicates, or activated calcium carbonates). In the non-reinforcing group, fillers such as clays, whittings, and barium sulfate are chosen for fabric coating compounds.
- Flame-retardant additives include halogen donors, and certain metallic oxides.

- Fungicides/antimicrobial agents may require incorporation into rubber mixes if the coated material is used in outdoor applications.
- Flavouring agents or odorants may sometimes be added into the rubber compounds for producing coated fabrics intended for use in hospital bedsheets and baby mats.
- Coupling agents are particularly necessary in some silica-based reinforcing fillers to improve filler-rubber interactions.
- Process oils are required to assist in the dispersion of fillers (reinforcing and non-reinforcing). They also promote tack to the compound, which may facilitate the coating operations.
- Antidegradants are important additives to incorporate in compounds to protect the finished goods from attack by atmospheric oxygen and ozone because these attacks are detrimental to most rubbers.

#### **5.5.2.2 Process Oils in Rubber Compounding**

The common softeners or process aids used as important ingredients in rubber compounding are mainly petroleum oils such as those of the aromatic, naphthenic and paraffinic group; these are available in different viscosities. To improve the processing behaviour of coating compounds, aromatic oils are generally suitable; naphthenic oils are suitable for high carbon black and high mineral filler-filled compounds and for coloured compounds; and naphthenic oils may be chosen because these oils are non-staining and are age-resistant [4]. The properties of different process oils are listed in **Table 5.2**.

<b>Table 5.2 Properties of rubber process oil</b>								
Type of oil	Specific gravity	Viscosity (c St) at 40 °C	Aniline point °C	Staining properties	Viscosity gravity constant	Flash point, open cup °C	Low-temp. behaviour	Storage stability
Aromatic	0.98	763.5	21	Fair	0.980	178	Fair	Fair
Naphthenic	0.95	110.2	71	Moderate	0.885	205	Moderate	Moderate
Paraffinic	0.88	19.7	96	Absent	0.809	230	Good	Good



When non-staining and non-discolouring compounds are made, the correct selection is paraffinic oils. In some cases, petroleum jelly may be incorporated as a softener in place of oils. This can also provide internal lubrication and give surface gloss to the finished product.

Characteristics such as (i) specific gravity (ii) volatility (iii) refractive index (iv) pour point (v) flash point, and (vi) aniline point are the common determining factors of the type of oil chosen (whether it is aromatic, naphthenic or paraffinic). The type of oil may be classified based on the viscosity gravity constant (VGC) according to norms set by the American Society for Testing and Materials (ASTM) [3]. The VGC of an oil can be calculated using the following equation:

$$\text{VGC} = \frac{G - 0.24 - 0.022 \log_{10} (V_2 - 35.5)}{0.755}$$

Where G = specific gravity at 15.5 °C

$V_2$  = Saybolt viscosity at 99 °C

The compatibility parameter of different oils in various rubbers such as NR, general purpose synthetic rubbers, and special purpose synthetic rubbers are given in Table 5.3 [8].

Table 5.3 Compatibility of process oils with various rubbers								
Type of oil	Type of rubber							
	NR	PBR	SBR	NBR	CR	EPDM	IIR	CSM
Aromatic	A	A	A	A	A	B	C	A
Naphthenic	A	A	A	B	B	A	B	B
Paraffinic	A	A	A	C	C	A	A	C
A: compatible; B: partly compatible; C: not compatible NR: natural rubber; PBR: polybutadiene rubber; SBR: styrene butadiene rubber; NBR: nitrile butadiene rubber; CR: chloroprene rubber; EPDM: ethylene propylene diene monomer; IIR: butyl rubber; CSM: chlorosulfonated polyethylene								

## **5.6 Mixing in a Two-roll Open Mill**

Two-roll mixing mills are the main ‘workhorse’ for the rubber processing industries. The machine comprises two parallel rolls made of alloy cast iron with chilled surfaces to provide high abrasion resistance and long service life. The rolls are fitted through bearings or gunmetal bushes in robust steel cast frames.

The driving arrangement of the machine to run the rolls is an electric motor coupled to a reduction gearbox. At the other end of the front and back roll, a pair of pinions are fitted which gives friction to the rolls. The friction ratio is calculated by the number of teeth provided on these two pinions. Hence, there is a speed difference between the two rolls. The back roll is running faster in comparison with the front roll, and the friction ratio of the rolls may be determined between 1:1.2 to 1:1.4 for rubber mixing. Sometimes even speed rolls are used in the warm-up mills to feed the calender machines.

Rolls rotate against each other at different friction ratios. They are made hollow or drilled from within to facilitate steam circulation for heating and cold water flow for cooling as the temperature rises during mixing. It is essential to regulate the temperature of the compound during mixing because heat is generated due to viscous flow inside the rubber in the nip of the rolls [5].

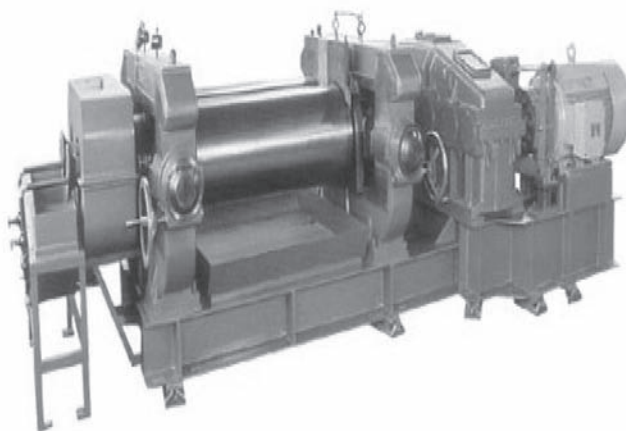
The friction ratio of the rolls of a mixing mill can be calculated using the following equation:

$$\text{Friction ratio} = \frac{\text{surface speed of rear roll}}{\text{surface speed of front roll}}$$

The speed of the front roll and back roll is determined by the number of teeth in the connecting gears fitted with the rolls at the other end.

For controlling the temperature in the water-cooling system, water enters and leaves the inside of the rolls through rotary union. Two types of rolls are deployed for a water-circulation cooling arrangement (core rolls and peripherally drilled rolls) which facilitate appropriate flow of water to exchange the heat generated. The desired mixing temperature is maintained to avoid premature vulcanisation or scorching of the compound.

Mixing is necessary to obtain a uniform dispersion of ingredients in the rubber bulk. A good mixing technique should ensure the incorporation of solid particles in the elastomer matrix. During mixing of a rubber, a good composition involves distribution and dispersion optimisation between the rubber(s) and compounding ingredients. A two-roll mixing mill with a driving unit is displayed in **Figure 5.4**.



**Figure 5.4** A two-roll rubber mixing mill

Reduction of viscosity and increase in plasticity during the mastication of NR and some of the synthetic rubbers in the mill-mixing process assists in incorporation of the additives.

The rubber mixing mill has a high power input. For example, a 40 cm diameter  $\times$  105 cm length roll mill requires a 45 kW motor to drive at a roll speed of 20-25 revolutions per minute (rpm), which can mix a batch size of 25 kg at a specific gravity of 1.25. A 55 cm diameter  $\times$  150 cm length mill requires a 95 kW motor to mix a batch size of 50 kg. The maximum roll size of a mixing mill is 65 cm diameter  $\times$  215 cm length, and the driving motor is required to run this machine at 185 kW.

A batch of 90-110 kg can be mixed in a single batch using this mill. It is advisable to use smaller batches for coating purposes to implement control while processing. The specifications of different sizes of two-roll mixing mills are listed in **Table 5.4**.

Table 5.4 Specification for two-roll mixing mills					
Specification	1	2	3	4	5
Roll size (diameter × length in inches)	12×30	14×36	16×42	18×48	22×60
Power (HP)	30	40	60	75	125
Friction ratio	1:1.18	1:1.18	1:1.22	1:1.22	1:1.22
Batch capacity max. (kg)	20	30	40	50	80

The mixing time required for completion is usually 30-40 minutes, but is dependent upon the size of the mixing batches. While mixing the rubber compounds in an open two-roll mill, the action of shearing, kneading and mixing of the rubber and the ingredients causes a difference in the friction ratio of the surface speed in the nip of the rolls. The adjustment of the roll nip gap can be done by moving the front roll by hand or a motorised device fitted to the mill.

A gap of ~6 mm at the nip is necessary to add rubber to start mastication of the rubber. After a few minutes of mastication and upon raising the temperature of the rolls, a band is formed on the roll surface.

Softening of the elastomer (natural or synthetic) takes place by mechanical action and heat or by chemical means using a small amount of peptiser which quickens the mastication process.

Gradual addition of powdered ingredients is needed to obtain a well mixed rubber. For synthetic rubbers, the elastomer needs to be heat-treated to ensure good mixing. If a tackifying resin is to be used, it is best to add it immediately after mastication. Dry fillers can be added with the process oil/plasticisers and this assists in the incorporation of the fillers into the mass, and finally the curing agents are added. A gradual increase of the nip gap is necessary, and the maximum nip gap can be adjusted to 12 mm when the mass of the compound is increased by the addition of ingredients.

Occasional cross-cutting by a hand knife by the mill operator and feeding back the stock while mixing are necessary for incorporation and blending.

To control the mill temperature, regular checking of the surface temperature of the roll and of the dump stock is important. Using an infrared non-contact thermometer

to measure the surface temperature is effective in comparison with the conventional thermocouple system.

In the preparation of a rubber compound for fabric coatings, it is necessary to disperse all the ingredients into the mix to attain a good flow with desired viscosity. This facilitates good adherence to the fabric substrate.

The processes in the mixing operation are:

- Plasticisation or viscosity reduction
- Incorporation
- Dispersion
- Distribution

For the mixing of coloured mixes, a separate area in the mixing department should be segregated to avoid contamination with black compounds. It is ideal to use a two-roll mixing mill because it is easier to clean than an internal mixer for coloured mixes. Various light coloured and brightly coloured rubber compounds (including white) are necessary to produce rainwear, snow jackets, air pillows, and airbeds. These mixes may be contaminated with the black in an internal mixer, which is difficult to clean.

A good compound preparation technique for a textile rubber coating is to ensure that all the compounding ingredients in powder or liquid form are dispersed homogenously to achieve good processing properties and to get a defect-free finished product. The friction ratio between the two rolls and the kneading action in the nip of the rolls are the decisive factors to obtain the appropriate dispersion.

Rubber compounds prepared in an open mill vary in properties, particularly from batch to batch. The probable causes of such variations can be categorised as:

- Incorrect selection of compounding ingredients.
- Improper mixing cycle.
- Improper blending of polymers when two or more rubbers are blended.
- Incorrect temperature control during mixing.
- Faulty order of incorporation of chemicals.
- Excessive batch size beyond the mill capacity.
- Improper dispersion of fillers and fine chemicals.

A familiar term used in the rubber processing industry is ‘bloom’ or ‘blooming’. Chemicals that may bloom in a rubber mix are sulfur, antioxidants, accelerators, oils, and waxes. It is due to their difference in solubility parameters compared with basic rubber. Blooming can create difficulties in adhesion with the substrate, and may degrade the appearance of a finished product when it exudes on the outer surface. To avoid this problem, it is suggested that combinations of such ingredients are used in the compound instead of using one ingredient at a higher dosage [10].

## **5.7 Internal Mixer**

Internal mixers or Banbury mills are deployed in rubber processing industries because they have high and rapid output and maintain a cleaner environment. An internal mixer of high intensity was invented by F.H. Banbury.

The Banbury mill is constructed with two cylindrical chambers with a rotor in each horizontal chamber. There is provision of cold water circulation all around the chamber periphery to control the temperature during the operation. The rotor designs are in two basic configurations: tangential and intermeshing types. These are provided with an arrangement of heating and cooling systems.

A feed hopper is provided with the machine – this is connected to a weighing chamber and is used for feeding the raw materials into the mixing chamber. The mixing module consists of mixing chambers, rotors and the drop door.

The complete assembly is mounted on a heavy metal bedplate. When the mixing materials are fed through the feed hopper, the pneumatically operated floating ram presses down the whole stock into the chamber, and the ram floats between 75 mm and 100 mm during the mixing operation. The speed of the rotors is maintained at 20-60 rpm according to the capacity and design of the machine. The prepared compound is ‘dumped’ through the drop door when the mixing is completed at a pre-determined time.

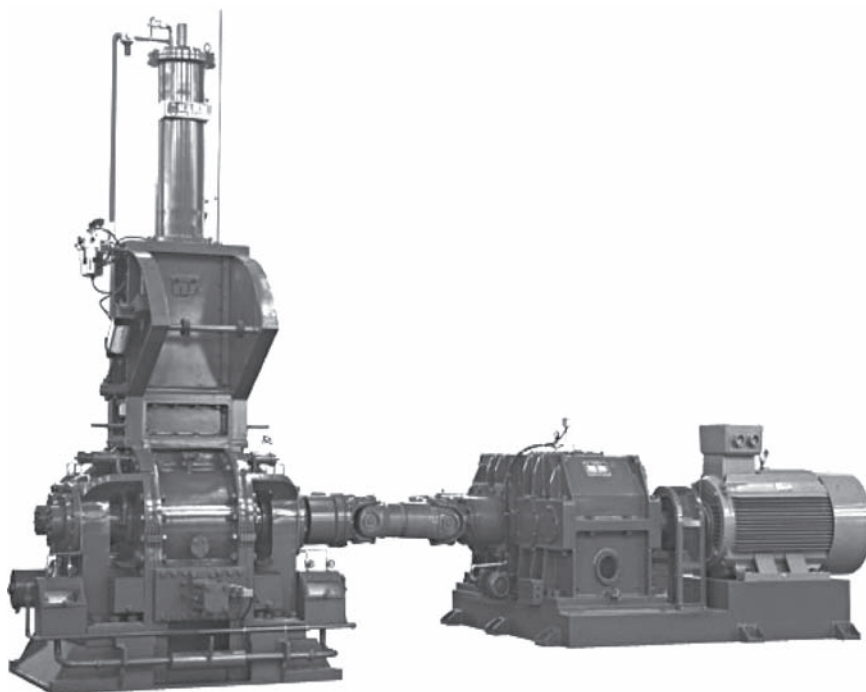
The time and temperature of mixing in an internal mixer are the important pre-ascertained criteria to terminate the mixing process to avoid over-mixing, batch-to-batch variation, and to maintain overall quality of the product. A batch up to about 200 kg can be mixed in a large size Banbury mill, so the control parameters must be precisely monitored [14].

In this machine, a high shear rate is obtained because of the small gap between the tip of the rotor and the chamber wall. Using intermeshing rotors, the mixing is also undertaken in the space between the rotors. To meet the increasing demand of rubber

processors, modified designs of the rotors are available for efficient and fast mixing processes. In a high efficiency machine, the dispersion and distribution of ingredients are made effectively and efficiently, and the mixing process can be completed within a cycle time of 3-5 minutes. An internal rubber mixer and its driving unit are shown in **Figure 5.5**.

A dumping two-roll mill is installed under an internal mixer to enable the addition of accelerators and curatives into the mixes. This is because the mixing is done at a high temperature in an internal mixer, and it is not safe to add curatives. This mill has other functions: to reduce the temperature of the dump stock, homogenise the mix, and to modify the viscosity.

In maintaining the consistency among the mixed batches, it is important to ensure the use of appropriate compounding ingredients at a correct weight and timing. Selection of chemicals must be followed strictly according to the formulation designed by the Technical Department.



**Figure 5.5** Internal mixer: Banbury mill

Precise control of: (i) elevation of the ram, (ii) opening of the hopper, (iii) mixing temperature, and (iv) final discharge at the end of mixing cycle is crucial. The degree of mixing is dependent upon minor ingredients being uniformly dispersed within the bulk of the major component.

The mixing operation is conducted in an internal mixer in a closed chamber. These have different designs with a very high abrasion-resistant wall, and have efficient cooling and heating arrangements.

Rotors are of tangential- and intermeshing-type design. The efficiency of mixing is dependent upon the design and placement of the rotors as well as the ram pressure (which is pneumatically operated 0.2-1.1 MPa). High efficiency machines are equipped with injection jets to add oils/plasticisers directly into the mixing chamber.

Control of the: (i) weighing of ingredients, (ii) opening of the hopper, (iii) charging into the mixer, (iv) elevation of the ram, (v) mixer temperature, and (vi) discharge at the end of mixing cycle can be done by automated means if a very high quantity of prepared compound is necessary.

It may also be an advantage to use an internal mixer because a clean environment can be maintained in the mixing department. This is because mixing is accomplished in a closed chamber, so the mixing is free from dust.

The problems that may be encountered during mixing in an internal mixer and subsequent processing of fabric coatings are:

*(a) Improper dispersion* can be due to:

- Improper batch size.
- Mixing time is inadequate.
- Order of addition of fillers and chemicals is not correct.
- High moisture in rubber/fillers.
- Ram pressure is insufficient.

*(b) Variation in batches* is caused by:

- Variation in rubber mastication.
- Improper dispersion of ingredients.
- Improper processing temperature.



- Variation in ram pressure.
- Incorrect time and temperature of dumping.

(c) *Scorching* is caused if the:

- Process temperature is too high.
- Cooling during mixing is insufficient.
- Vulcanising agents not appropriately dispersed.
- Dumping temperature is excessive.
- High speed of rotor.

Scorching or premature vulcanisation is a major problem in a rubber processing factory, and the coating industry is no exception (particularly during calendering). Compounders as well as processors should take care while designing a recipe suitable for safe processing. Sometimes seasonal changes in the recipe (especially in the curing agents) may be needed for safe rubber compounding [15].

In general, the problem of scorching can be attributed to the following:

- Imperfect design of the compound.
- Uncontrolled processing temperature.
- Improper cooling before storage and at processing stages.
- Defective processing equipment.

## **5.8 Rheology and Processability of Rubber Compounds for Textile Coatings**

Appropriate reduction in viscosity and an increase in the plasticity of the basic elastomers facilitate mixing and subsequent processing necessary for the fabric coatings. Mechanical milling in an open two-roll mixing mill or in an internal mixture can be done to complete this process. This primary process is essential for the appropriate incorporation of compounding ingredients. The processability of mixes plays a major part in giving shape to the final product. Inappropriate processing performances may create problems during mixing, calendering or vulcanisation. Processability testing is an important requirement for the development of the product.

In rubber processing industries such as producers of rubber textile-coated products, there is great demand for a high rate of output because in the course of calendaring a high rate of power consumption is needed for mixing, warming and handling. Therefore, there should be fewer rejected products, minimum scrap materials in the processing system, and control of the materials being processed.

The uniformity of materials at each step of production can be processed efficiently. Uncontrollable behaviour of unvulcanised compounds during processing may be observed. The major concern of the coating industry is the mixing and safe processing methods; measurements can be established on the ingredients (e.g., raw polymers and chemicals) and the degree of mixing.

To circumvent the problems seen during processing in the elastomer fabric coating industries, the following precautionary measures can be taken [16]:

- All input raw materials and prepared rubber compounds should be characterised at different stages of the production process.
- The measurement should be closely associated with the conditions of processing or the basic characteristics of the rubber molecules.
- The testing methods should conform to the manufacturing operations in the actual processing conditions, and should be understandable to the shop-floor operators. Use of instruments and methods which rapidly perform tests are effective.
- A combination of these control methods may increase material efficiency, efficient use of input energy, and economic utilisation of the equipment.

### **5.8.1 Mooney Viscometer Test**

The Mooney viscometer can be used to ascertain the processing behaviour of the raw rubber and the mixed composition, which is related to the average molecular weight. The Mooney viscometer is considered to be the most useful test for the processability for raw stock and the compounded form. For assessing raw rubbers, the value of the Mooney viscometer test is the benchmark.

The American physicist and rheologist Melvin Mooney (1893-1968) developed the Mooney viscometer to measure the change in elastomer properties from the uncured state to the cured state. Samples may be taken from the compound prepared for further processing and can be tested in this instrument.

In this apparatus, the specimen is deformed by a rotating plate that determines the change in viscosity at a preset temperature. In addition, accurate data can be taken

throughout the test. The rotor speed provided in the device is 2 rpm, the usual temperature is set at 100 °C. The time is a minimum of 60 minutes, the air pressure is 0.4 MPa, and the range of viscosity is within 1-200 Mooney units [10]. A standard Mooney viscometer is displayed in **Figure 5.6**.

Computer software may be integrated which can configure the various tests, and printed test reports can be obtained from such machines as a reference for further processing of the material. The machine is provided with two types of rotors (large and small) which are suitable to test raw rubber-to-rubber compounds.



**Figure 5.6** Mooney viscometer

### **5.8.2 Rheological Study of Rubber**

Rheology is the study of flow and deformation of a rubber compound interrelated with stress, strain, and time. It is dependent upon the temperature and chemical composition

of the rubber compound. A rheological test is important to the rubber processing industry to assess the characteristics of the material taken up during production as well as its rate of deformation at a particular temperature. To determine the problems anticipated during processing (e.g., mixing, warming-up, calendering), this test can be efficiently conducted on compounds by the processor.

In rubber-to-textile coating processes, different elastomers (or a combination of two or more rubbers) are blended to obtain specific product properties and to achieve improved processing. Along with the basic rubbers, other ingredients need to be incorporated. This makes the rheology studies difficult. Different rubbers may exhibit pseudo-plastic behaviour, which may provide erroneous data.

Rheology is the study of the deformation and flow of materials when a stress is applied. A viscous material such as rubber can dissipate all the energy as heat to viscous resistance, and its flow is irreversible [15].

### **5.8.3 The Rheometer**

A rheometer determines the selected vulcanisation characteristics of prepared rubber compounds. It is necessary to check the processing behaviour and curing of every batch of rubber compound prepared for further processing (e.g., calendering, extrusion, spreading) to control the quality of the mixed batches. The tests can characterise the various samples to ensure that subsequent processing is optimal.

A rheometer can be selected for run timing and torques; tests can be monitored from a computer. The latest machines have computer software programmes that can configure various tests of different samples [15].

Customisable reports can allow for the determination of different parameters and multiple charts and tables. In general, the oscillating frequency is 100 cycles per minute and the oscillation amplitude is 2°. The temperature processor can be set up to 200 °C and can be selected to match the processing temperature. The air pressure required for operation is 0.4 MPa [10].

A rheometer with computer control is shown in **Figure 5.7** and an ideal rheograph is illustrated in **Figure 5.8**.



**Figure 5.7** Oscillating disc rheometer. Reproduced with permission from Qualitest, Fort Lauderdale, FL, USA

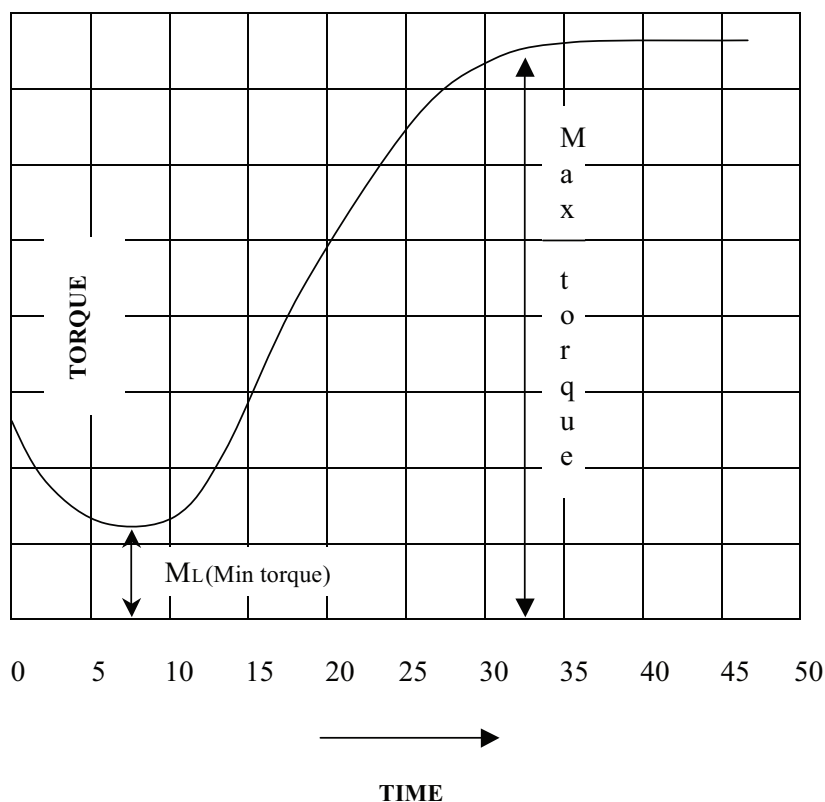


Figure 5.8 An ideal rheograph of a rubber compound

## 5.9 Rubber Coating of Textiles

In the processing technology of coating textiles, there are two basic methods employed in the industry:

- A wet system, and;
- A dry system.

The coating of textiles is the process whereby a polymer layer is applied to one or both sides of the fabric surface to enhance the performance of the material.

Care must be taken for adherence of the elastomeric coating with the textile base. If a thin coating is required or an anchor coating is applied before the subsequent coatings to increase the layer thickness, the dipping or spreading system is appropriate.

On finishing the coating operation, the coated material is cured in a steam heated vulcaniser in roll form or in a long press under pressure between heated platens in sections. Press curing is suitable if thickly coated fabric is required to be cured. In a machine curing system, the Rotocure™ machine is used to vulcanise both sides of coated or plied coated textiles (particularly if thicker technical rubber-coated materials are to be cured). High adhesion strength is essential between the plies when a technical elastomeric-coated textile is to be produced.

In general, the elastomer-coating industry makes coated fabric in woven textiles for domestic and technical uses. However, in many technical and other applications, knitted, and non-woven fabrics need to be coated. During the coating process of lighter fabrics, there is the chance of distortion along the weft line and curling on the selvage border (the problem of curling selvages in knitted fabric is more pronounced). To avoid this problem, during the application of rubber coating, care should be taken with respect to the tension arrangements fitted with the coating equipment and also to adjustment of the speed of stretching during coating [17].

### **5.9.1 Wet System of Coating Textiles**

Aqueous-based coating systems and water-dispersible polymers can be applied on to fabric. After coating, the water present in the composition is evaporated by passing the coated fabric in a hot air oven or in a drying machine where air is heated indirectly through a heating chamber. Using this process for coating technical fabrics, the fabrics are fully immersed in an aqueous-based polymer composition. The impregnated fabric is squeezed in a pad mangle to a constant pick-up after calculating the coating weight based on dry fabric weight. It can then be dried in a hot air stenter fitted with a mechanical system for maintaining the width of the dried finished fabric, and can be rolled on a batching roller.

If it is necessary to coat one side of the fabric, then the fabric is passed over the top lick roll rotating at a specific speed to control the coating amount picked up by one side of the fabric.

In a solution coating system, the prepared rubber compound is dispersed in an organic solvent (or mixture of solvents) to prepare a viscous dough that can be applied to the fabric surface in a rubber-spreading machine.

For a solution dipping or dough-spreading system, the prepared dry rubber compound is swelled in solvent for  $\geq 12$  hours. The swollen material is then transferred to a solution mixer (e.g., rubber solution kneader) to prepare the spreading dough of specific viscosity.

A single- or double-arm horizontally installed Sigma kneader is the equipment used to prepare viscous dough by kneading and mixing the rubber compound and solvent for use in the coating of fabric on a spreading machine. The dough is processed between sigma blades and the container. A cooling arrangement is provided with a jacket and circulation of the water inside the blades. The jacket minimises the temperature increase that may occur during kneading to avoid scorching of the rubber solution.

The rubber to solvent ratio for preparation of the spreading dough is maintained at 1:4. For use in a solution dipping system, the solution is prepared at a lower viscosity whereby the proportion of solvent is much higher in comparison with solid content [9].

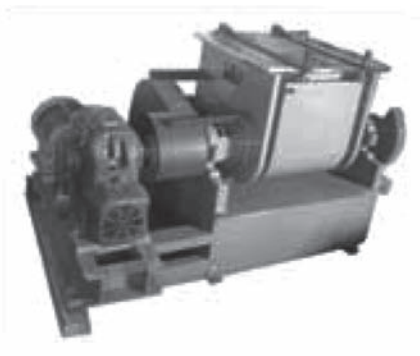
The technical specification of sigma kneaders utilised for the preparation of rubber dough is given in **Table 5.5**.

<b>Table 5.5 Specification for rubber solution kneaders</b>	
<b>Total volume capacity (litres)</b>	<b>Power of driving motor (horsepower)</b>
25	3
60	5
125	10
225	20
500	30
1000	60
1500	75

After running for a specific period of time, depending on the type of elastomer, the container of the solution kneader is tilted by a hydraulic cylinder to discharge the dough.

The sigma kneader is available in various designs and capacities from 5 litres to 200 litres with a driving motor of 1.5-56 kW. The actual working capacity of the machine is 60% of the total volume of the container. A sigma kneader unit and its standard 'Z' blade are shown in **Figure 5.9**.





(a) Sigma kneader for the preparation of rubber dough

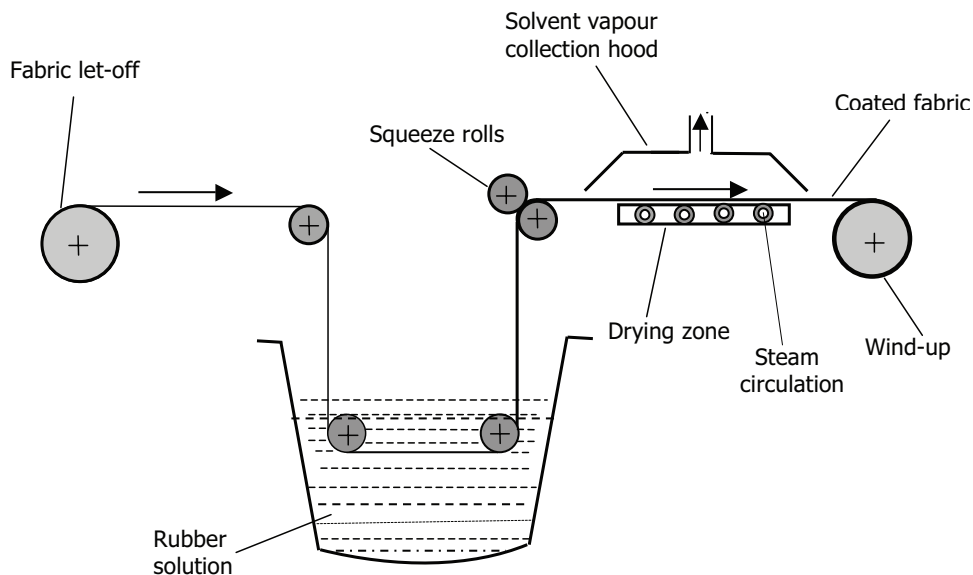


(b) 'Z' blade for a sigma kneader

**Figure 5.9** Components of sigma kneaders

The vertical rubber solution mixer is also used for the preparation of coating solutions if less viscous coating needs to be prepared. Such low viscosity solutions are usually administered in the dipping system of coatings.

In the dipping process of coating, the viscosity of the rubber solution should be maintained at a low level to facilitate penetration of rubber solution into the fabric. A schematic representation of a rubber dipping plant for coating fabric is illustrated in **Figure 5.10**.



**Figure 5.10** Textile dip coating unit

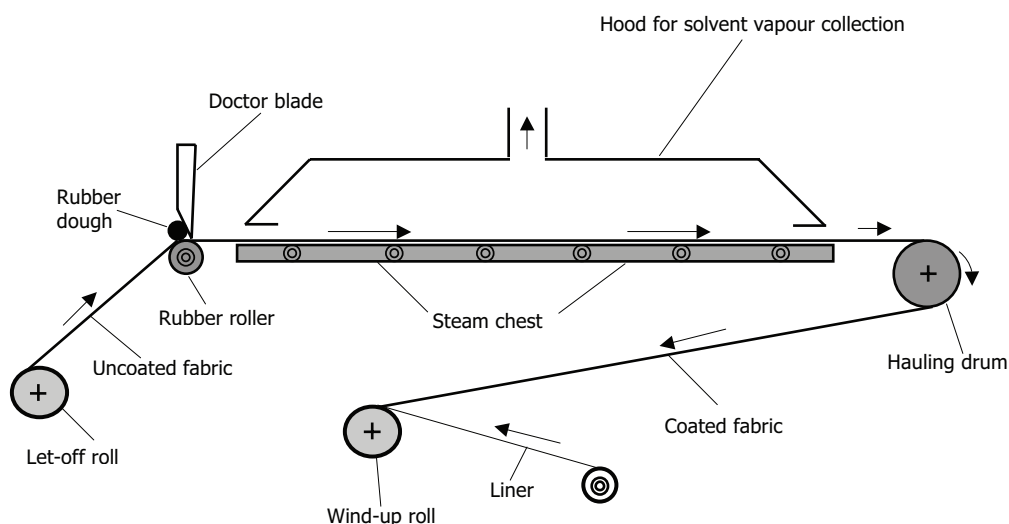
Intended for the solution coating method, the solvent is used at 40% by weight in comparison with the solids. Excess solvent is evaporated while the coated material is passed through a heating zone fitted just after coating, heated with a thermal fluid system or by using steam.

In the spreading system, the coating thickness can be adjusted by regulating the gap of the Doctor blade on the rubber roll. The angle of positioning of the knife is also a considerable factor in the penetration of the rubber solution into the fabric interstices.

The solvent vapour is collected and adsorbed upon passing into a vessel filled with activated charcoal (the segment of the solvent recovery plant). Adsorbed solvent is then heated with thermic fluid or steam, and passed into a cooling vessel where the vapour is condensed to a liquid solvent.

In the final stage, the condensed solvent is collected in drums and can be reused. If a solution coating system is used, care should be taken with using highly flammable solvent in the preparation of the dough while passing through the heating chest, as well as simultaneous accumulation of static electrical charges. This may create a high risk of explosion and fire due to the build-up of inflammable solvent vapour.

To minimise this risk, safe working conditions and an automated process control must be established. Increasing the humidity in the atmosphere of the workshop by setting up a high efficiency, fine water sprinkler can help to minimise the risk of fire.



**Figure 5.11** Rubber-spreading machine (schematic)

Highly efficient electrical earthing devices must be installed in every spreading machine for preventing the risk of electrical sparks that might catch fire [18]. A schematic diagram of a rubber spreading unit is shown in **Figure 5.11**.

### **5.9.2 Latex Coating**

Using the wet method, coatings can be applied on textiles using latex mixes (usually on carpet backings) by spreading or spraying. The latex, when dried after coating, anchors the pile of the tufted carpet. Application of latex compounds by a lick roller system on to the back of the carpet at a controlled position enables partial penetration of latex to hold the piles. If operated in a spreading process controlling the speed and tension of the carpet, the weight and angle of the blade should be the crucial technical parameters [5]. For providing anti-skid properties to the carpet backing, the application of foamed latex compounds gives good results. Woven fabric can be

dip-coated with latex mixes using the dipping method, but difficulties will arise due to the drying of water in the latex mix. Passing the coated fabric through a forced hot air circulation tunnel may be the answer to this problem.

In the compounding of NR latex, dry fillers can be added to the mix by preparing dispersions in soft water using a ball mill. Aqueous dispersions of the chemicals (e.g., accelerators, pigments, surface-active agents) necessary for processing can also be added to the latex. Heat sensitive coagulants for foamed carpet backings are added to latex mixes [19].

## **5.10 Technology of Calendering on Fabric Coatings**

The dry system of rubber coatings is used with the calendering technique to coat a wide variety of fabrics. In comparison with the wet process, this method of coating is more economical. Using costly solvents is a major part of the wet process, and they are evaporated during coating. Considering the rate of output, the calendering system is much faster in comparison with the wet spreading system. Nevertheless, the cost of the robust construction of the calender machine and its power consumption make it much more expensive to run the plant in comparison with a spreading system.

The coating of textiles in a rubber calendering machine involves converting an elastomeric compound to a continuously pressed viscous elastomer compound on continuous sheets of fabric. Effective and defect-free coating is associated with the viscosity of the rubber compound, speed of rotation of the rolls, friction ratio, and gap of the nip. Temperature, pressure, and rate of shear also affect the quality of output.

Rubber calendering machines are made in a wide range of sizes: dimensions are considered based on the length and diameter of the rolls. A machine of roll size 0.3 m diameter  $\times$  0.9 m length can coat at a speed of 9 m/min of a fabric of maximum width 0.8 m, and the driving motor required is 18 kW. The maximum roll size available for rubber coating is 0.6 m diameter  $\times$  1.8 m length, it can coat a maximum width of fabric of 1.7 m at a speed of 9 m/min, and the driving motor required to run the machine is 93 kW. The speed of output can be altered depending upon the product requirement [5].

Different sizes of rubber calendering machines and their output capacity are listed in **Table 5.6**.

Table 5.6 Rubber calender sizes and capacities			
Roll size (diameter × length in inches)	Approximate output speed (m/min)	Width of coated product (inches)	Driving motor (horsepower)
12 × 36	9	30	25
14 × 42	9	36	40
16 × 48	9	42	50
18 × 54	9	48	60
22 × 66	9	60	100
24 × 72	9	66	125

### **5.10.1 Technical Prerequisites of Calender Machine Rolls**

The calender rolls actually carry out the coating. Therefore, they must conform to the highest quality standards when the rolls are being made for use in calendering machines. Rolls are manufactured out of high quality chilled cast iron to obtain the appropriate hardness, excellent surface finish, outstanding abrasion resistance, and appropriate resistance to deflection in preventing deformation while rubber compounds are processed (particularly if high hardness mixes are required).

The rolls of calendering machines are very heavy components. They therefore require a strong frame support (which is usually constructed from cast steel or high-grade cast iron). The frame also supports the heavy-bearing blocks. These must withstand the high nip pressure (500-1,000 kN/m) generated by the processing of the material through the nip. Various technical advantages of modern calendering machines are available because these machines are fitted with anti-friction bearings [2].

Effective heating and cooling should also be taken into consideration if the basic material is selected to manufacture calender rolls, as well as the coring or drilling the inner periphery of the rolls.

To maintain the uniformity of thickness of the coated material throughout its width, crowning or cambering of the rolls is needed to compensate for the deflection during operation of the machine. The rolls are ground thicker at the middle than at the ends. Depending upon the size of the rolls and the nature of product to be processed, the amount of cambering is applied in a positive or negative manner.

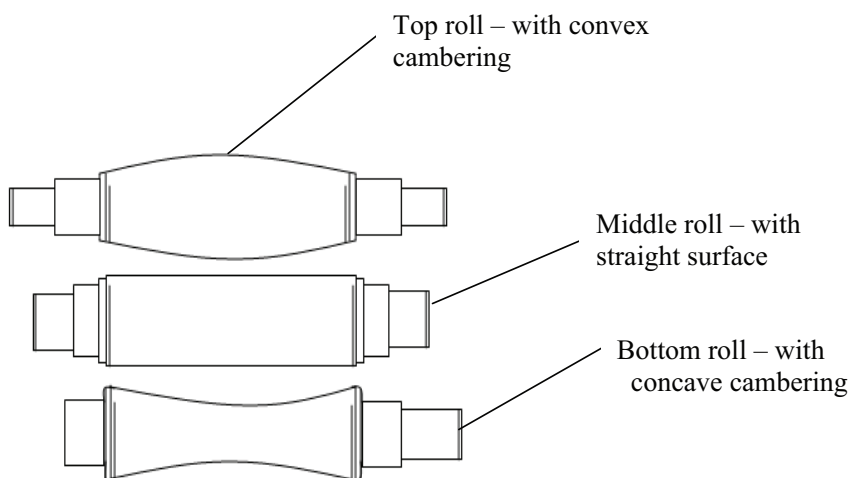
To cover the wide range of product processing using different types of rubber compounds, cambering should be done on the basis of the average dimension. Adequate profiling of rolls and provision of roll-bending devices compensate for deflection under load that contributes in maintaining a uniform thickness of the coating along its width [20].

#### **5.10.1.1 Roll Deflection and Coating Uniformity**

Manufacturing coated fabric of uniform dimensions and thickness in warp and weft directions is important for economical operation as well as for technical reasons in the making of various precision engineered items.

However, achieving such perfection is difficult. This is because a small deflection of the calender rolls occurs due to their weight and further consequences of deflection result when they are loaded with the rubber compound. The convexity of the top roll and concavity of the bottom roll may help counteract this problem. Nevertheless, these kinds of corrections of the roll deflection are suitable for a limited range of compound variations. A superior system of controlling this problem in a rubber calendering machine is known as the 'swivel-roll' or 'cross-axes' machine. A special type of bearing is fitted to the machine to allow the axis of the top roll to move slightly in relation to the middle roll to provide a space of opening to the nip at the ends of the rolls that is slightly higher than at the centre [20].

Feeding uniformly with a warmed compound of specific plasticity will assist in maintaining thickness uniformity. Using a cold feed extruder instead of manual feeding by dollies will provide good results in controlling thickness. Feeding by oscillating back and forth using extruder feeding (similar to the movement of a pendulum across the nip) is ideal to obtain the correct thickness of the coated material. Calender rolls with convex and concave cambering are displayed in **Figure 5.12**.



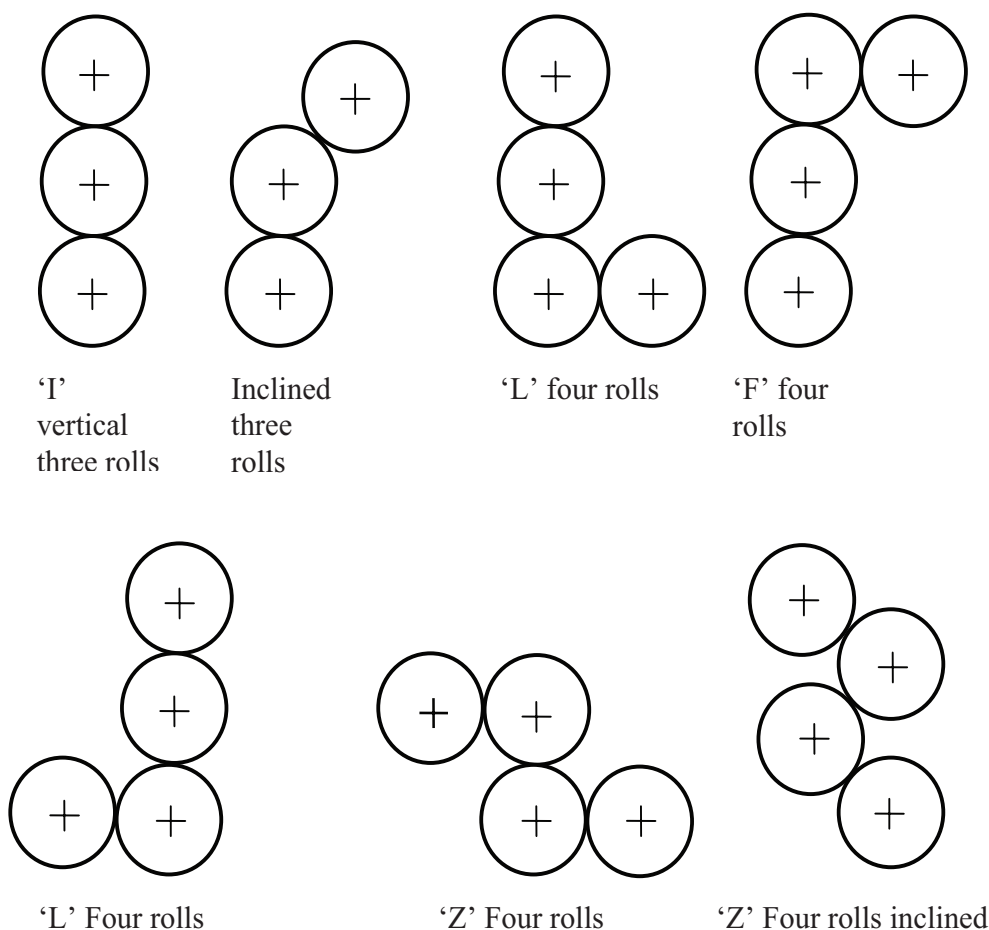
**Figure 5.12** Cambering of calender rolls for a three-roll calender machine (exaggerated view)

### **5.10.2 Arrangements of Calender Rolls and their Operational Requirements**

Rubber calendering machines for coating textiles are available in different configurations. They are usually designed to facilitate coating in the positions of (i) vertical arrangement (ii) inclined position or (iii) Z-arrangement. The calendering machines are made according to the specific requirement of the users.

To operate a rubber calendering machine, the roll arrangements are made in the manner described next:

**‘I’ arrangement:** this three-roll vertical configuration is utilised for the friction coating of textiles and coating of one side of the fabric in one run. Compound dollies are fed from the warm-up mill to the first nip, and the fabric passed between the second nip.



**Figure 5.13** Configuration of calender rolls 'I' 'L' and 'Z' Arrangements of three- and four-roll machines

'F' design: this four-roll arrangement is used to coat both sides of the fabric in a single run. The thickness of the coating can be maintained from 0.1 mm to 2 mm. Feeding is at the first and third nip as the fabric is passed through the second nip. This configuration facilitates easier feeding of the compounded dollies when one surface of the fabric is coated.

'L' arrangements: this four-roll machine is designed to facilitate the feeding. The operation is easier for calendering unsupported and supported sheeting with greater accuracy of thickness.



'Z' arrangements: this four-roll composition in the manner of the English letter 'Z' is most suitable for coating both the surfaces of the substrate at one run. Because of the lower height of the machine, the machine can be operated without difficulty [2].

Different patterns of roll configurations in three- and four-roll rubber calendering machines are demonstrated in **Figure 5.13**.

### **5.10.3 Calendering for Coating**

A large number of products are made by combining rubber and various types of fabrics. Therefore, the method of rubber impregnation of fabric is an important manufacturing process conducted with the help of a calendering machine by following the dry system of textile coating. The prepared rubber compound for the textile coating operation shall have good flow behaviour and softness. These work well in this process to make intimate contact with the fabric's substrate and adhere firmly.

Rubber calendering machines are designed and made according to the requirement of the user and the product to be manufactured. Hence, the rate of output may increase according to the need and type of product being coated. High performance calendering machines for coating are equipped with auxiliary devices (e.g., thickness controller, temperature controller, handling systems) to facilitate the operation of fabric coating. Such modern calendering units greatly improve the quality of the calendered product whereby a single-layer coating or a double-layer coating are processed in a single run [21].

#### **5.10.3.1 Three-roll Calendering**

In a three-roll calendering operation, pre-warmed dolly rolls or small rolls of rubber compound from a warm-up two-roll mill are fed into the first nip and a rolling bank is formed in the roll nip runs around the middle roll. This roll revolves at a friction ratio of 1:1.5 in comparison with other rolls. A pre-dried fabric is passed into the second nip. The rubber compound having sufficient tack makes a continuous film because the velocity of the middle roll is higher than that of the other rolls.

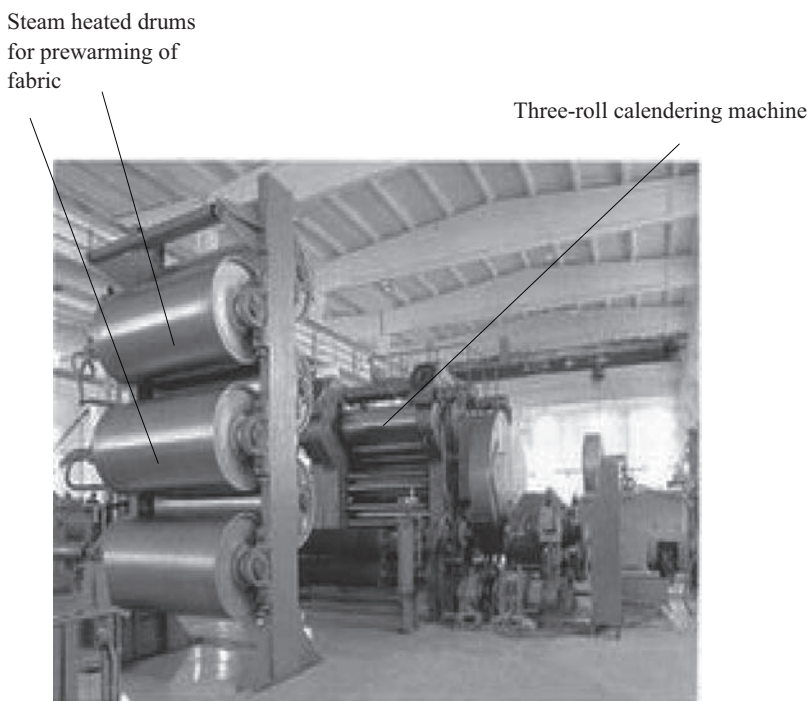
Adjustment of the nip gap by a motorised device in-between the centre roll and the lower roll determines the desired thickness of the coating taking into consideration the basic fabric thickness. The deposition/formation of thickness is dependent upon the type of fabric and the nature of the prepared rubber compound. A second/separate pass is required for coating both surfaces of the fabric.

In a three-roll calender, one side can be coated at a time. If a coating is required on both surfaces, the one-side coated fabric may again be introduced to coat the reverse side. Before feeding, the fabric for calendering must be preheated by passing through steam heated drums to get better adhesion to a moisture-free surface (particularly for cotton-based fabric).

For synthetic fabric, pretreatment (RFL dip) or application of a base coating with a suitable bonding agent (isocyanate or proprietary bonding agent) mixed with a rubber solution is necessary to obtain specific adhesion with the substrate. An on-line system of cooling rolls may be installed behind the machine to cool the coated fabric when it comes off the calender to eliminate various defects (e.g., premature curing, blisters, porosity) and to avoid sticking.

After sufficient cooling of a fabric that is coated on both sides, it is then dusted manually by a brush on a long table or by a mechanical device with a dusting agent (e.g., starch powder/talcum powder). After dusting, the coated material is rolled on hollow metal drums and vulcanised in steam heated autoclaves without using a liner, which may leave an impression on the rubber-coated surface.

The complete calendering unit of a three-roll calendering machine with fabric warming rolls is displayed in **Figure 5.14**.



**Figure 5.14** A three-roll rubber calendering machine: a complete set-up for fabric coating

#### **5.10.3.2 Four-roll Calendering Unit**

A four-roll calender set-up is utilised to coat both sides of a fabric in a single operation when the rubber bank is fed on the first and third nips of the rolls. Fabric is passed through the second nip and the rubber layers are formed on both surfaces at one run. Using a four-roll machine, it is possible to make two different colour coatings on two surfaces using two different coloured rubber mixes in two nips for processing (e.g., for rubber-based hospital sheeting).

In the process of coating industrial and technical fabrics, to achieve sufficient adhesion between the substrate and rubber layer, a pre-impregnation step or friction coating is necessary. Examples are tyre cords, conveyor belts and other coated technical fabrics to make inflatable items. For this operation, a friction ratio of 1:1.1 to 1:1.2 is maintained in the first nip and second nip that forces the rubber into the fabric weave.

For friction coating, it is important to ensure that the rubber goes into the interstices of the fabric. Rubber compounds for friction coatings must have high tack and low viscosity because a portion of the material should stick to the roll surface to achieve better frictioning otherwise it will result in a topping layer remaining on the fabric surface.

It is also imperative to adjust the roll temperature to get the adequate viscosity of the compound for providing good adhesion, but care should be taken to avoid scorching of the compound. Depending upon the requirement, the calendering speed can be maintained at 10-20 m/min along with adjustment with the rate of output.

For these high output machines, manual feeding from a warm-up mill may not be adequate; installation of a roller head extruder to feed the calendering machine directly in the nip area may be necessary. Preheating and feeding of rubber compounds to high-output calenders is also done through cold feed extruders to improve processing. To get smooth calendering and good surface finishes of the coated material, the influence of the rubber compound is a considerable factor during coating.

The ‘memory effect’ or the elastic recovery appears after calendering, this occurs due to a too nervy rubber compound being used. It affects the shrinkage of the calendered material, and may appear perpendicular to the direction of calendering. Correct mastication of the elastomer, selection of suitable fillers, and other processing aids are incorporated into the mixes to avoid this problem and to get a smooth surface finish of the calendered materials [2].

When a rubber composition is prepared for use in coating textiles by a calendering system, to avoid processing problems during the operation, the following precautions should be observed:

- Control of excessive shrinkage (this predominates if calendered rubber sheets are made without support, but is also observable during the coatings of rubber fabric).
- Non-sticking to the calender roll at the processing temperature.
- Provide sufficient surface tack for the fabrication of articles from coated material.
- Appropriate scorch safety.

#### **5.10.4 Control of Temperature in the Calender Rolls**

It is critical to control the heating and cooling system of calender rolls during the coating operations to get the desired calendering properties. The adjustment of

temperature also varies according to the nature of the basic elastomer in the rubber composition. Two types of rolls are used in rubber calendering machines to obtain efficient heating and cooling systems:

- Cored rolls
- Peripherally drilled rolls

In cored rolls, steam is circulated for initial heating of the rolls, and cold water circulated to lower the temperature when the temperature increases beyond the specified processing temperature. For peripherally drilled rolls, the channels provided under the surface of the rolls impart faster heating and cooling to the roll surfaces.

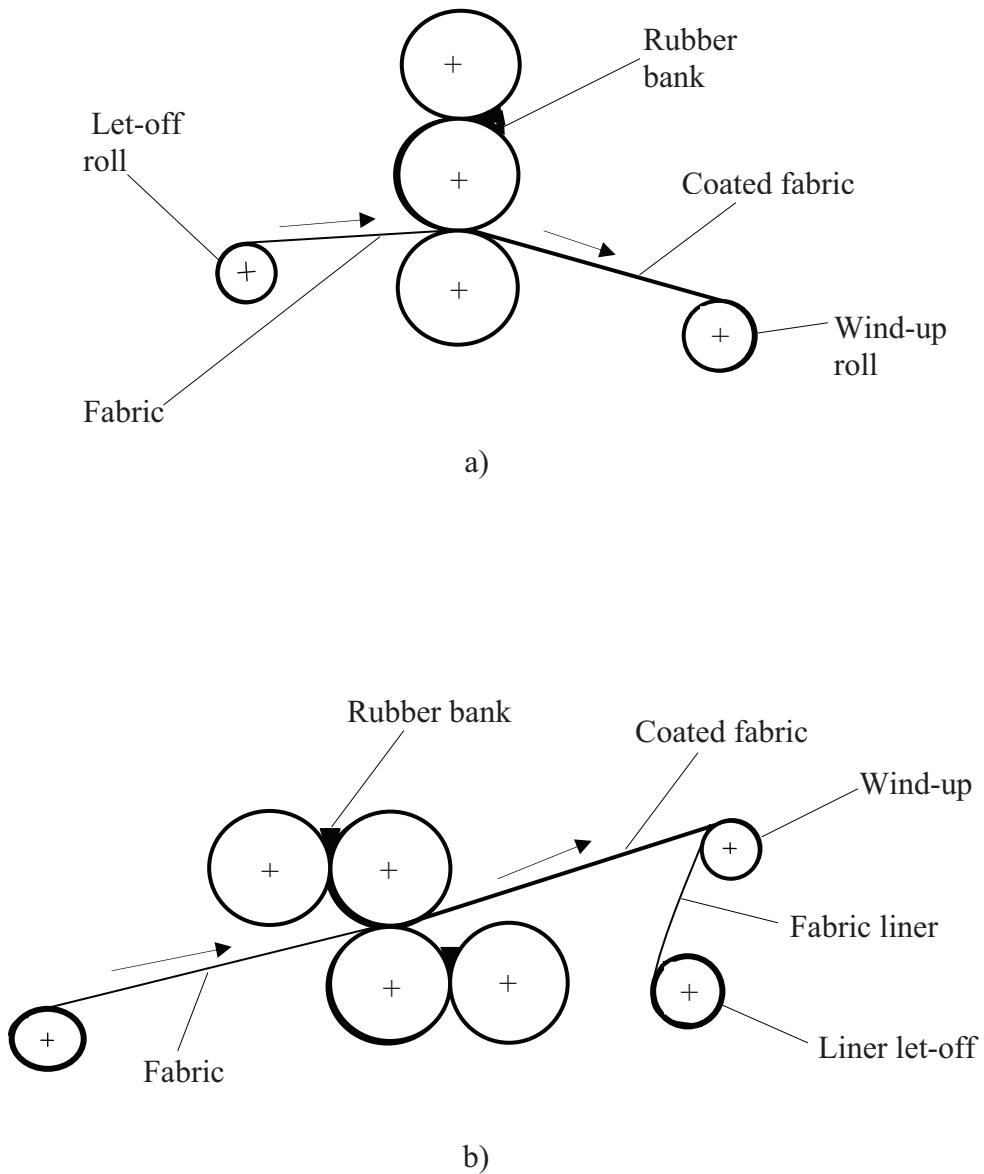
The temperature can be controlled within a tolerance of  $\pm 1$  °C throughout the working surface of the rolls if an efficient heating and cooling system is accessible. Such precise control of temperature may be necessary during calendering to process some high-tech textile rubber-coated products [2, 20].

Three- and four-roll calendering machines under operation are illustrated in Figure 5.15.

#### ***5.10.5 Thickness Measurement and its Control in Calendering***

Measurement of thickness and its control is a significant operation during coating in a rubber calendering machine. The thickness of the calendering material may vary from point-to-point during the run. This needs adjustment from time to time by regulating the temperature of the rolls or adjusting the gap of the nip of the roll.

Devices are used to measure and control the thickness of the coated sheeting. The manual pressure foot thickness gauge is a common device for a calendering machine operator to use to periodically check the thickness of the sheeting during coating. If adjustment is necessary, it can be done by adjusting the nip gap using a motorised device fitted to the machine.



**Figure 5.15** a) Three-roll calendaring (coating on one side of the fabric); b) four-roll calendaring arrangement (both sides coating at a time)

Modern instruments have been developed to measure the articles on non-contact systems. The devices of mechano-electrical systems can scan the surface of the

product with a mechanical sensor and thickness gauges installed at different points for indication of the thickness [20]:

- *β-ray thickness gauges*: work based on the transmission or reflection principle. Using this device, the difference between a known input intensity of rays, and the intensity of rays leaving the system is used to measure and control the sheet thickness. This is because the amount of radiation transmitted is directly proportional to the weight per unit area of the rubber sheet. The instrument can depict the weight per unit area, variations in sheet dimensions, and the thickness variation in the longitudinal direction.
- *Electromagnetic devices*: a reference roller is used to fix the position of the surface of the sheet. The measuring head is an electromagnetic gauge, which varies the magnetic signal with changes in sheet thickness.
- *Electropneumatic devices*: the pneumatic pressure corresponding to a position is compared with the actual pressure that changes due to variation in the sheet thickness in a pneumatic system.

#### **5.10.6 Problems Encountered During Calendering**

The processing difficulties arising during coating in a calendering machine depend greatly upon the nature of the mixed rubber compounds. Nevertheless, faulty machines are also responsible for creating defects in the product [2].

Some of the common problems encountered during the operation and their probable causes are described next:

- Variation in coating thickness may be caused by incorrect roll crowning, and the wearing down of roll-bearing journals in old machines.
- Bending device is not correct.
- Blistering occurs because of a too-high roll temperature, larger feeding bank and longer warming-up time.
- Porosity is due to the presence of moisture or volatile chemicals in the rubber compound or it may be in fillers or in the elastomer itself. This problem may also occur during processing, frequent cutting and folding in a mixing mill, and during feeding to the calender.
- Scorching – ineffective control of temperature; bank feeding is too large; warm-up stock stored for a longer time; heat history of the compound that is under processing.

- Coating peeling off – fabric not properly warmed up; improper process temperature; improper feeding; incorrect roll crowning; roll pressure not adequate.
- Crushing and distortion of fabric – these problems appear due to high roll pressure; crowning of roll is not appropriate; weak fabric construction.
- Friction picking-off – this problem is because the temperature of the roll is not appropriate; improper tack of the compound; incorrect roll speed (friction ratio).
- Crow's feet – this problem emerges because of a low roll temperature, improper warming up of the compound, high nip force between the centre and bottom rolls of a three-bowl calender.
- Calendering effect – perpendicular shrinkage to the direction of calendering due to strong elastic recovery of the rubber compound, the compound is nervy due to improper mastication.

## **5.11 Methodology of Vulcanisation of Coated Fabrics**

Vulcanisation (or curing) is the process by which the reaction between the rubber and sulfur results in greatly augmented elastic properties, and protection of the properties over a comparatively wide temperature range. It is an established technique in which the basic ingredients of a vulcanising system are sulfur, a base oxide, and chemical accelerators. A standard practice of adding fatty acids such as stearic acid further activates the vulcanisation process. The system is used in NR and many synthetic rubber compounds.

Sulfur links up rubber molecules at many points along their length and as a result elasticity in the cured material is developed.

Polymer chains of an unvulcanised rubber are joined together or crosslinked by sulfur bridges to give a three-dimensional network which provides increased elasticity to the cured product. During vulcanisation, a network of combined sulfur is formed in many ways. The crosslinks may be present as monosulfide, disulfide and polysulfide linkages, as well as pendant sulfides [4].

The effect of crosslink density on the physical properties of elastomers is shown in **Figure 5.16**.

When a rubber composition is prepared, various other ingredients are incorporated in the rubber stocks (e.g., fillers, process oils, process aids, protective agents). These can contribute to the physical properties in cured rubber and assist in processing, but do not take part in vulcanisation.



In some elastomers, peroxides are incorporated as the vulcanisation agent. They generate free radicals that can crosslink a wide variety of saturated and unsaturated elastomers. Peroxides create strong carbon–carbon type crosslink bonds that allow the elastomer to obtain its physical potential. The benefit of better heat-ageing properties can be obtainable in peroxide cure systems. However, high elongation, higher tear strength, and better flex fatigue properties can be accomplished with sulfur cure systems [10].

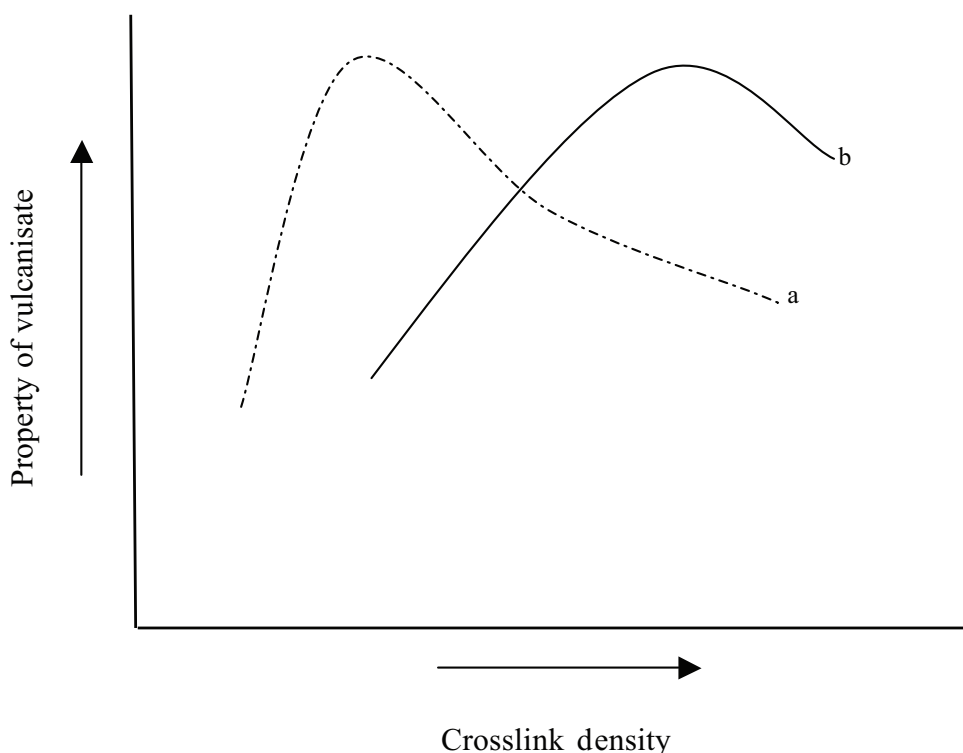
Speciality rubbers such as CR are vulcanised with metallic oxides such as zinc oxide and magnesium oxides included in the mixes for curing.

To carry out vulcanisation, heat is applied at shorter or longer durations of curing for the conversion of a plastic material to an elastic substance, and pressure is applied for the retention of the shape and dimension of the product. The vulcanisation of thinly coated rubberised fabric may not require pressure; circulation of hot air ('festoon cure') can cure these stocks effectively. However, care should be taken at the compound designing stage regarding the probable ageing of the rubber surface used in this method of curing.

An elastomer-coated fabric becomes a flexible, complex material by applying coating compounds on one face or both faces of the textile substrate. The coated fabrics are then: (i) autoclaved in roll form (ii) festoon-cured in chambers for thinly coated fabrics (iii) rotation-cured in a machine (iv) press-cured in long lengths (usually for thicker-coated fabrics).

Predominantly in the fabric rubber-coating industry, a huge stock of materials is required to vulcanise in bulk. Hence, the economics of vulcanisation plays an important part in the cost of the finished products. To operate a safe and effective curing system of textile rubber-coated materials, the following parameters must be taken into consideration:

- Vulcanisation should be cost-effective.
- Obtaining a product with improved performance characteristics by modifying vulcanisation chemistry.
- Care of the environment, health and safety should be taken.



**Figure 5.16** Physical properties and crosslink density. a) Tear strength and b) tensile strength and toughness

### **5.11.1 Festoon Curing**

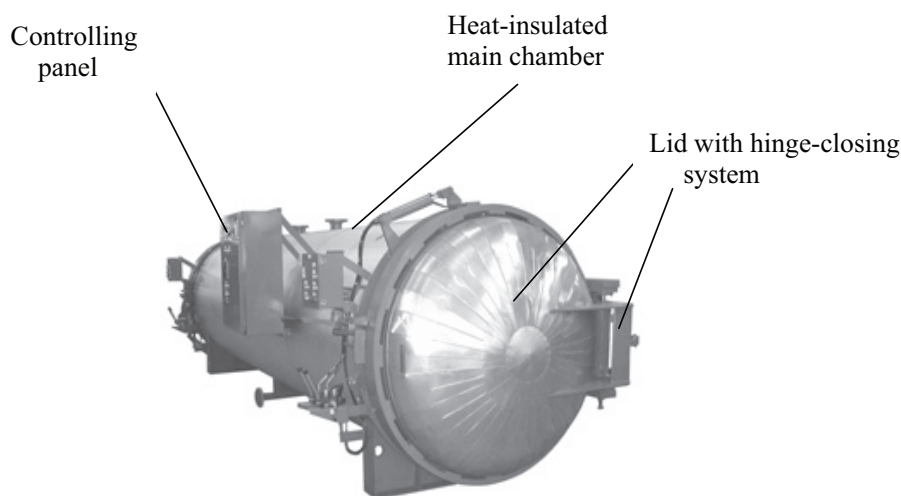
This is a method of vulcanisation of rubber-coated fabrics based on the nature of the coated stocks. To cure thinner-coated textiles, the ‘festoon’ stove cure system is appropriate. In this method of curing, a thin coating on one side or both sides of the fabric can be cured without application of pressure in a large heat-insulated chamber constructed of metal sheets.

Unvulcanised coated fabric is suspended like festoons on metal hangers fitted on a big trolley. The loaded trolley (which is stationed near the heating chamber on metal rails) is then driven inside the festoon chamber, and the doors of the chamber locked manually.

The festoon chamber is fitted with metal tubes along its walls and roof for heating by circulation of steam. A batch of 300-500 m of coated fabric can be cured for a given time at 120–130 °C. Hot air is circulated inside the chamber by operating an electric fan. The total time taken to complete vulcanisation of a batch at atmospheric pressure is 2.5-3 hours. The cured fabric is then cooled by circulation of air, inspected and sent for subsequent fabrication when necessary.

### **5.11.2 Autoclave Curing**

If a thicker, DT-coated fabric or two-sided coated materials are to be cured, a length of 30-40 m coated fabric is wrapped on higher diameter metal drums after dusting with anti-sticking dusting powder (usually talcum/starch powder). Alternatively, fine close woven fabric can be used as liner for both sides of coated fabric to prevent sticking during vulcanisation. Usually 10-12 of such drums are placed together inside a vulcaniser. The rolls can be cured using the indirect steam heating method. The steam is circulated through metal tubes fitted along the walls of the vulcaniser. The total curing time is usually 1.5-2 hours at 135-140 °C. Compressed air is supplied by an air compressor to build up pressure (0.3 MPa) within the vulcaniser [11]. The materials are cured under air pressure and temperature generated by the supply of steam to the heating coils. A rubber vulcaniser utilised for coated fabric curing is shown in **Figure 5.17**.



**Figure 5.17** Rubber vulcaniser

### **5.11.3 'Step' Curing System**

An effective way of reaching the vulcanisation temperature slowly inside the festoon curing chamber (or in an autoclave after charging the products for curing) is to specify a period of 'rise' before the vulcanisation stage. This signifies that the temperature of the chambers is elevated gradually from room temperature to the final curing temperature, and that the temperature is 'held' for a specific period until vulcanisation is complete. This system of 'step' curing procedure can be effectively controlled by installing time and temperature controllers.

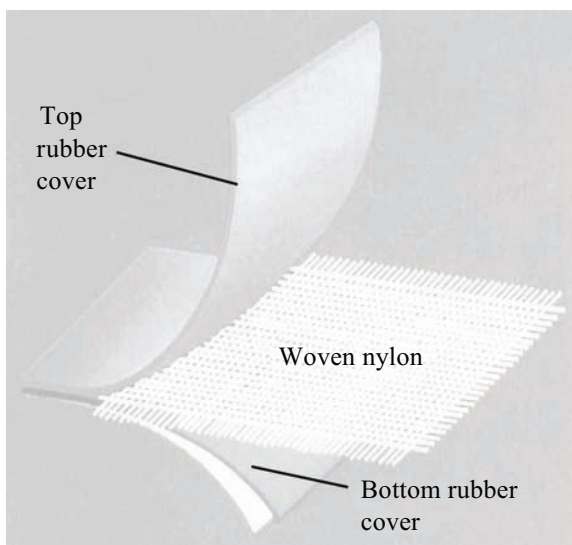
Electronic controlling devices are available to record the complete operation of curing by drawing graphs on printed graph paper about the progress of temperature during vulcanisation. This instrument can be installed outside the vulcanisation chambers. A few samples of rubber-coated fabrics are shown in **Figure 5.18**.

### **5.11.4 Press Curing**

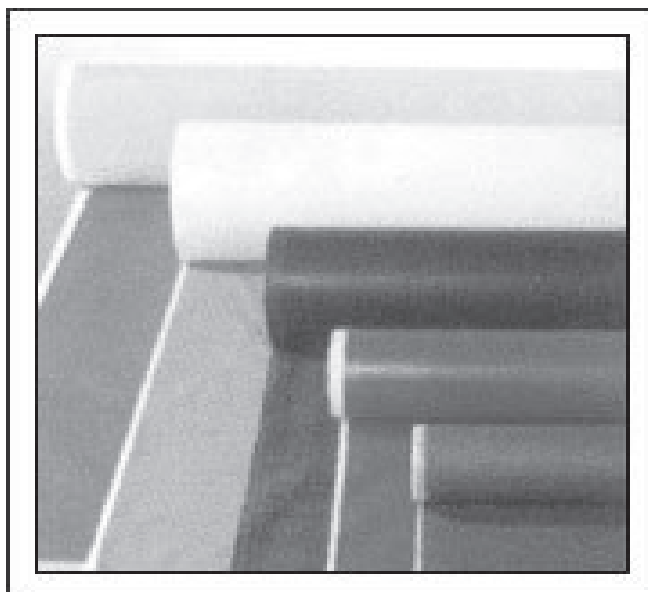
Rubber coated materials of higher thickness can be cured in long flat multi-ram presses with a single- or double-daylight system. If very high adhesion strength is required in technical coated fabrics (especially for engineering applications), press curing is ideal. Sufficient pressure can be applied during vulcanisation using a hydraulic press.

Hydraulic presses of steel-frame construction, 3-5 m in length fitted with steam heated platens as well as hydraulically operated multi-ram systems can be utilised to cure high-thickness single- or multi-ply-coated products.

Thicker rubber-coated products such as flat belts, conveyor belts, rubber-coated glass textiles, and other high-thickness coated technical textiles can effectively be cured in steam heated presses.



a)

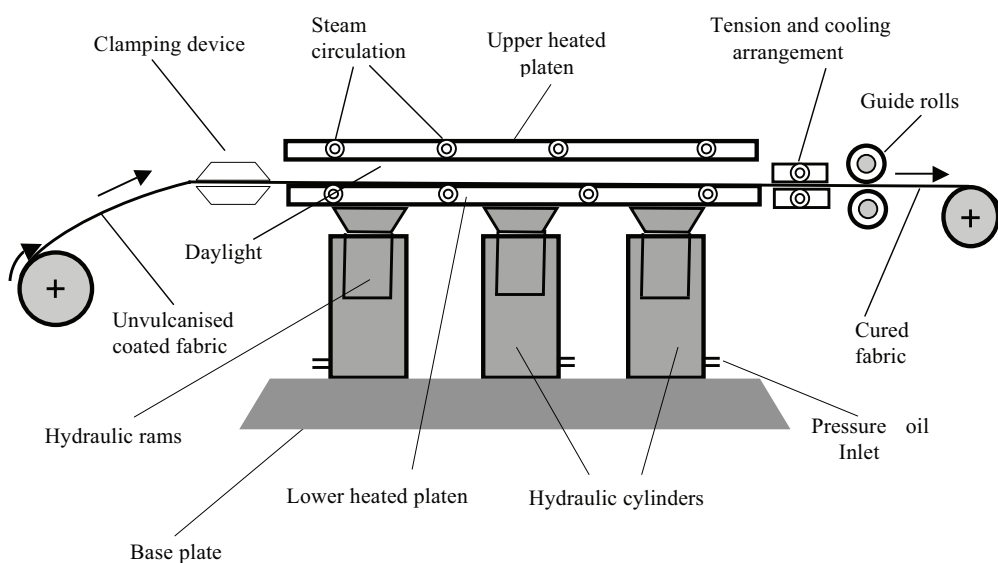


b)

**Figure 5.18** a) Coated Nylon (magnified view); b) coated fabric in different colours

This curing system uses the procedure of ‘curing in sections’ whereby the coated material is unreeled from a ‘let-off’ roll stationed close to the press, and a longitudinal section is vulcanised in the press. In the same way, the second section is cured, and the process is continued until the whole length is complete. A cooling zone is provided with the press to prevent overcuring between consecutive sections of the coated material. The press is also equipped with a stretching device (usually consisting of flat, hydraulically operated clamps). The coated material is stretched to a given amount before closing the press to avoid the appearance of wrinkles of the cured item at its edges. This stretching process is important to prevent excessive increase in the coated material that may occur during service (particularly if used in constructing inflatable engineering items) [1].

A hydraulic press for the section-curing system of rubber-coated materials is illustrated in Figure 5.19.



**Figure 5.19** Hydraulic press for coated-fabric curing (schematic)

#### **5.11.5 Rotocure System (Continuous Cure)**

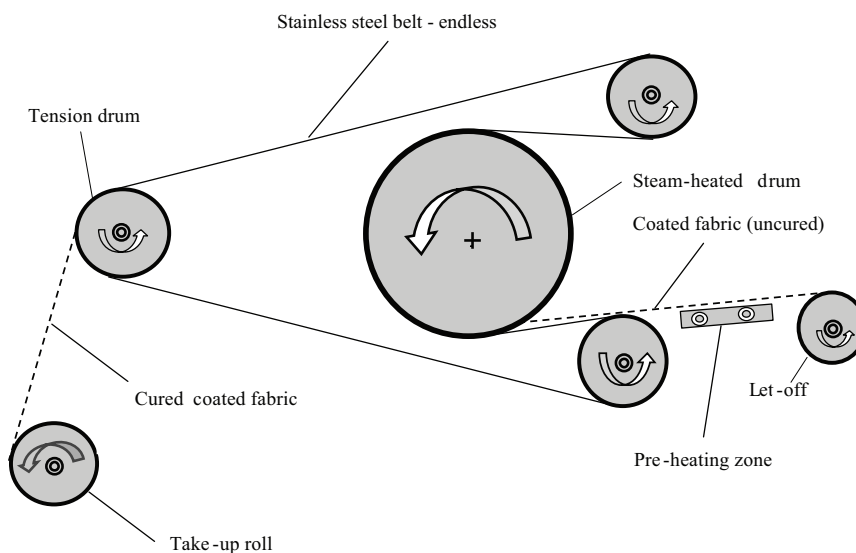
This is a method of continuous drum curing for the vulcanisation of rubber-coated textiles. Green uncured coated stock is wrapped on a metal drum, passed through

a preheating zone and escorted to tension rollers that ultimately lead into the nip, which is held between the large heated drum and a steel tension belt. This belt holds the coated sheet around the heated drum.

The end of the steel band is maintained under tension and positioned tight against the drum. The steel band and the drum are heated together upon supply of steam by running the machine free for some time before charging with the material for curing. When the unit achieves the desired temperature, the coated material is fed to the nip, and heated while passing through the preheated zone. Furthermore, due to the pressure of the heated steel belt on heated drum, the coated material is vulcanised [1].

This method of continuous curing can cure long lengths of coated fabric or even rubberised flat belts or conveyor belts upon adjusting the speed and temperature of the machine.

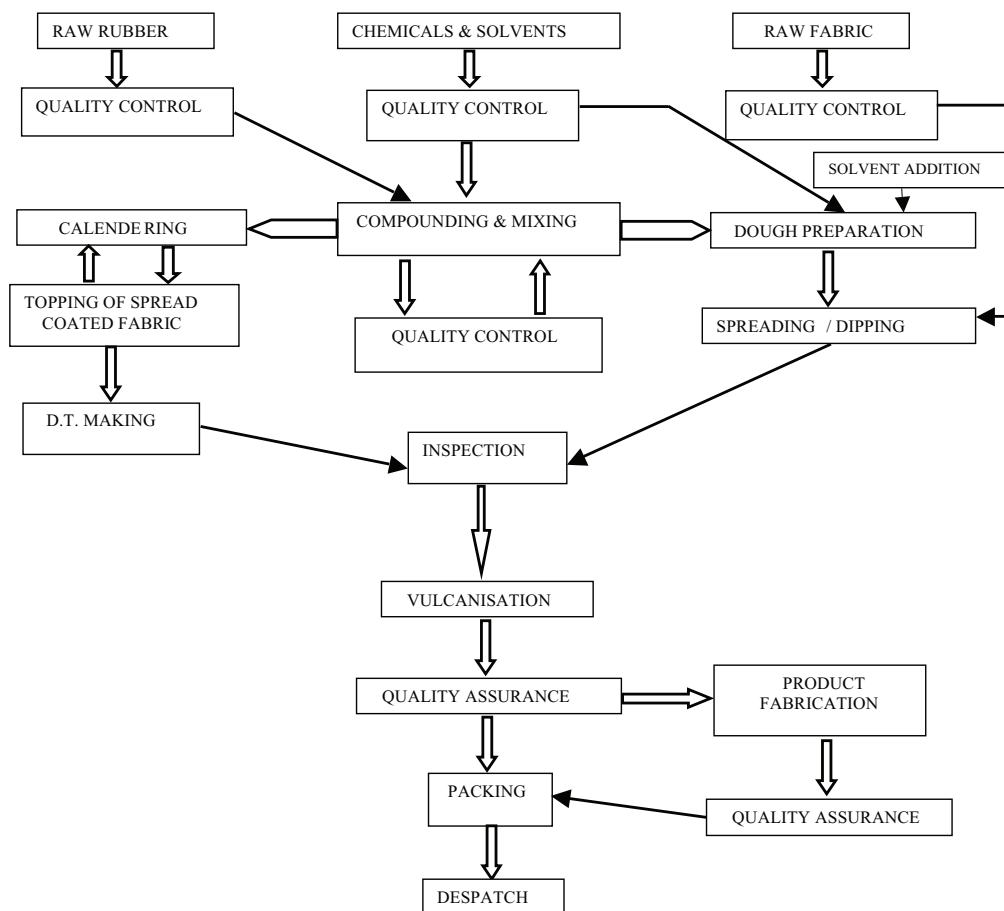
The Rotocure machine is used to cure rubberised materials. It is usually provided with a stainless-steel belt of width 1.5 m, and the diameter of the main drum is 2 m. The curing speed of the drum is controlled at 10-20 m/h depending on the thickness of the material. This speed can be slowed down to 5 m/h; the maximum pressure is maintained at 5 kgf/cm<sup>2</sup>. The cure time can be set from 5 minutes to 50 minutes. Moreover, material of thickness  $\leq 30$  mm can be cured using this system [1]. A typical Rotocure plant is illustrated in Figure 5.20.



**Figure 5.20** Rotocure machine for continuous cure

In this continuous-cure machine, a high temperature of vulcanisation is used (165-170 °C) because the contact time for curing is less. In such situations, care should be taken with respect to the reversion or thermal degradation of rubber that may occur to the coating compound due to high temperature of curing. Selection of elastomers and design of the rubber compounding recipe should overcome this problem during curing.

An outline of a manufacturing flow chart for rubber-coated fabric is shown in Figure 5.21.



**Figure 5.21** Manufacturing flow chart for rubber coated fabric



## **5.12 Some Suggested Formulations for Rubber Coated Fabrics**

Designing a formulation for a particular product is an art. The compounder must have thorough knowledge about the chemical and physical characteristics of the ingredients incorporated in the compound and should have an awareness about the product's ultimate end use.

Development of a formulation for a coated fabric should primarily be to provide trouble free processing and to offer the ultimate product quality. As the manufacturing of the coated fabric undergoes different processing stages, knowledge of ingredients and their effectiveness in the final compound are essential.

To formulate a recipe for coated fabric is particularly intricate, because a number of technical points need to be considered when a recipe is prepared. The properties of the end product required by the end-user have to be considered and a product which can provide the desired service life is also needed.

Appropriate compounding for producing coated fabric of different category where the major consideration is the product cost and shall provide trouble free processing behaviour in workshop scale. Selection and use of proper additives can offer considerable variation in the end product properties; as well as may affect the processing characteristics in the factory and its handling during manufacturing processes.

The main objective of the preparation of an effective recipe for a coated fabric is to produce a specific end product. To accomplish this task successfully, use of research and development work and laboratory data are always significant for the development of the product and its transfer to factory processing.

Usefulness of different rubbers in particular applications and the details about various compounding ingredients have been discussed in **Chapters 2 and 3**.

Formulations recommended for the manufacture of some kinds of coated fabric are given in **Tables 5.7-5.10**.

<b>Table 5.7 Natural rubber and SBR-based: black fabric coating</b>			
<b>Ingredient</b>	<b>Base coating spreading (phr)</b>	<b>Solution dipping (phr)</b>	<b>Calender sub-coating (phr)</b>
Natural rubber	100.00	100.00	80.00
SBR-1502	--	--	20.00
Renacit VII	0.35	0.35	0.25
CI resin	4.00	4.00	3.00
PF resin	2.00	2.00	--
Zinc oxide	5.00	5.00	5.00
Stearic acid	1.00	1.00	1.00
Struktol A60	--	--	4.00
Brown factice	--	--	10.00
FEF carbon black	15.00	10.00	25.00
Whiting	20.00	20.00	15.00
Precipitated calcium carbonate	--	--	15.00
China clay	--	--	20.00
Antioxidant TQ	1.00	1.00	1.50
Paraffin wax	--	--	1.00
Aromatic process oil	5.00	5.00	6.00
Retarder	0.20	--	0.50
Cyclohexylbenzothiazole sulfenamide	0.80	1.00	1.00
TMTD	0.20	0.10	0.10
Sulfur	2.50	2.50	2.50
Cure: 2 h at 3.00 kg/cm <sup>2</sup> steam pressure in vulcaniser in rolls wrapped on metal drums FEF: Fast extrusion furnace carbon black TMTD: Tetramethyl thiuram disulfide			

Table 5.8 Natural rubber and SBR-based coloured fabric coating		
Ingredient	Base coating (phr)	Calender sub-coating (phr)
Natural rubber	100.00	75.00
SBR-1502	--	25.00
Renacit VII	0.30	0.25
Titanium dioxide	5.00	5.00
CI Resin	5.00	4.00
Zinc oxide	5.00	5.00
Stearic acid	1.00	1.00
Retarder	0.20	0.20
White factice	--	10.00
Struktol A60	--	4.00
Activated calcium carbonate	--	20.00
Precipitated silica	10.00	10.00
Precipitated calcium carbonate	--	15.00
White China clay	15.00	20.00
Barytes	--	10.00
Antioxidant SP	1.50	1.00
Wingstay L	--	1.00
Paraffin wax	--	1.00
Aromatic process oil	5.00	8.00
PEG	2.00	2.00
MBTS	1.00	1.00
TMTD	0.10	0.10
Sulfur	2.50	2.50
Rubber colour	--	2.00
Cure: 1.5 h at 3.25 kg/cm <sup>2</sup> steam pressure in vulcaniser in rolls PEG: Polyethylene glycol MBTS: Dibenzthiazyl disulfide		

<b>Table 5.9 High weather and chemical-resistant fabric coating</b>		
<b>Ingredients</b>	<b>Calender base coating (phr)</b>	<b>Calender sub-coating (phr)</b>
Hypalon 40	80.00	90.00
PBR 1220	10.00	10.00
Chlorinated rubber	10.00	--
Magnesium oxide	5.00	5.00
Stearic acid	1.50	2.00
Antioxidant NBC	--	1.50
Litharge	10.00	10.00
SRF black	15.00	--
FEF black	--	25.00
Calcium carbonate	15.00	20.00
Dark factice	--	10.00
Petroleum resin	4.00	2.00
Phenolic resin	2.50	2.00
Diocetyl phthalate	15.00	10.00
MBTS	0.50	0.50
Tetrone A	2.00	2.00
Cure: in Rotocure at 155 °C at 10 m/h SRF: Semi-reinforcing carbon black Antioxidant NBC: nickel dibutyl dithiocarbamate Tetrone A: dipentamethylene thiuram hexasulfide		

Table 5.10 Polychloroprene base coating	
Ingredient	phr
Neoprene GRT	95.00
PBR 1220	5.00
Light magnesium oxide	4.00
Stearic acid	0.50
Petroleum resin	5.00
FEF black	30.00
Fine silica	10.00
Dark factice	10.00
Aromatic process oil	10.00
Pine tar	3.00
PEG	2.00
Antioxidant TQ	1.50
Phenyl- <i>p</i> -phenylenediamine	1.00
MBTS	0.30
Ethylene thiourea	0.30
Zinc oxide	5.00
Cure: Rotocure at 155 °C at 15 m/h	

CR compounds may be soaked in a toluene and xylene blend (70:30) for  $\geq 12$  hours. The mixture is then transferred to a 'Z' blade mixer with additional solvent and the total solid content is maintained at 40%. The prepared dough at a specific viscosity can be applied on the bonding agent-treated synthetic fabric on a spreading machine. For the calender, application of a base coating can be prepared with less filler, and can be applied on the fabric as an anchor coat before subsequent calendering.

In CR compounds – red lead ( $\text{Pb}_3\text{O}_4$ ) is used instead of magnesium oxide and zinc oxide for water-resistant compounding. Greater processing safety can be achieved if combinations of diphenyl guanidine and tetramethyl thiuram monosulfide with a small dosage of sulfur replace the accelerator ethylene thiourea [22].

### **5.12.1 Oil Resistant Coating**

The rubber compound which provides high oil resistance property can be prepared from nitrile rubber with a high ACN content. Prepared dry compound is swollen in a solvent mixture of methyl ethyl ketone and ethyl acetate blend at a ratio of 50:50 for 24 hours. The spreading dough can be prepared in a 'Z' blade solution kneader with the addition of more solvent and run for 6 hours to prepare the dough. The dough should contain  $\geq 40\%$  solids. Coating can be undertaken in a spreading machine. For thicker coating, the number of coating operations must be repeated [11]. A recipe for a high oil resistant coating is given in **Table 5.11**.

<b>Table 5.11 High oil-resistant coating by spreading</b>	
<b>Ingredient</b>	<b>phr</b>
Nitrile rubber (41% ACN)	100.00
Pepton 22	0.50
Zinc oxide	5.00
Stearic acid	1.00
CI resin	6.00
SRF black	25.00
Precipitated silica	10.00
Sulfur	1.50
Antioxidant PBN	1.50
Antioxidant 4020	1.00
DEG	2.00
DBP	15.00
MBTS	1.50
TMTM	0.25
Cure: Hydraulic press cure for 20 minutes at 155 °C (in sections) DBP: Di-butyl phthalate DEG: Diethylene glycol	

### 5.12.2 High Waterproof and Weather Resistant Coating

Usually the ethylene propylene diene monomer (EPDM) is chosen to make high waterproof as well as high weather resistant coatings, because the elastomer offers the desired properties. The EPDM coated textiles are generally used for making of tarpaulins, tents and high water proof coverings for outdoor services. It shows the properties of high flexibility resistance to heat, resistance to ultraviolet light, oxygen, ozone and to natural degradation, hence accepting its suitability for use in hostile environments. The characteristics of EPDM rubber are discussed in **Chapter 2**.

A recipe for EPDM based fabric coating by calendering is illustrated in **Table 5.12**.

Table 5.12 EPDM-based fabric coating (calendering)	
Ingredient	Calender coating phr
EPDM (medium ethylidene norbornene)	100.00
Zinc oxide	5.00
Stearic acid	1.00
Petroleum resin	5.00
PF resin	3.00
FEF black	30.00
Activated calcium carbonate	25.00
Naphthenic oil	20.00
MBT	2.50
TMTD	1.00
Zinc dibutyl dithiocarbamate	1.50
Sulfur	2.00
Cure: in rolls for 3 hours at 4 kg/cm <sup>2</sup> steam pressure in a vulcaniser	

### 5.12.3 Heat-Resistant Textile Coatings

For producing heat-resistant coatings, a recipe can be prepared for various applications using butyl- and silicone-rubber based compounds. Graphical representation of the heat-resistant properties of different rubbers is given in **Figure 5.22**.

It has been observed that some compounding ingredients may degrade synthetic fabrics such as Nylon and polyester (the most widely used reinforcing fibres in rubber-coated textiles products). These tend to contain moisture at higher temperatures. The rate of degradation of polyester increases during vulcanisation at 150 °C. This is influenced by water in the presence of amine groups in the chemicals of rubber mixes. This causes considerable loss in the strength of the fibres. Disorientation of Nylon fibres may occur in the presence of a small amount of moisture at 175 °C. Therefore, care should be taken in the selection of compounding ingredients, avoidance of moisture, and setting of curing temperatures while producing heat-resistant textile-coated materials [3].

The recipes based on butyl rubber and silicone rubber for heat-resistant coatings are detailed in **Tables 5.13** and **5.14**.

<b>Table 5.13 Butyl rubber coating (heat-resistant)</b>	
<b>Ingredient</b>	<b>phr</b>
Enjay butyl 218	100.00
Zinc oxide	5.00
Stearic acid	0.50
Durez resin 31671	5.00
Paraffinic process oil	15.00
Antioxidant B	1.50
SRF carbon black	40.00
Precipitated silica	10.00
DEG	2.00
MBT	1.50
Tellurium diethyl dithiocarbamate	0.50
Zinc dimethyldithiocarbamate	0.50
Sulfur	1.50
Cure: 3.5 hours at 145 °C in a vulcaniser	
Durez resin 31671: phenolic resin	
Antioxidant B: acetone and diphenylamine condensate	



Table 5.14 Silicone rubber coating on glass fabric (heat-resistant)	
Ingredients	phr
Silicone rubber (SE-421)	100.00
Fumed silica	5.00
Zinc oxide*	3.00
Benzyol peroxide (50%)	1.50
Cure: Hydraulic press cure for 25 minutes at 160 °C (in section)	
*Zinc oxide improves tack and adhesion	

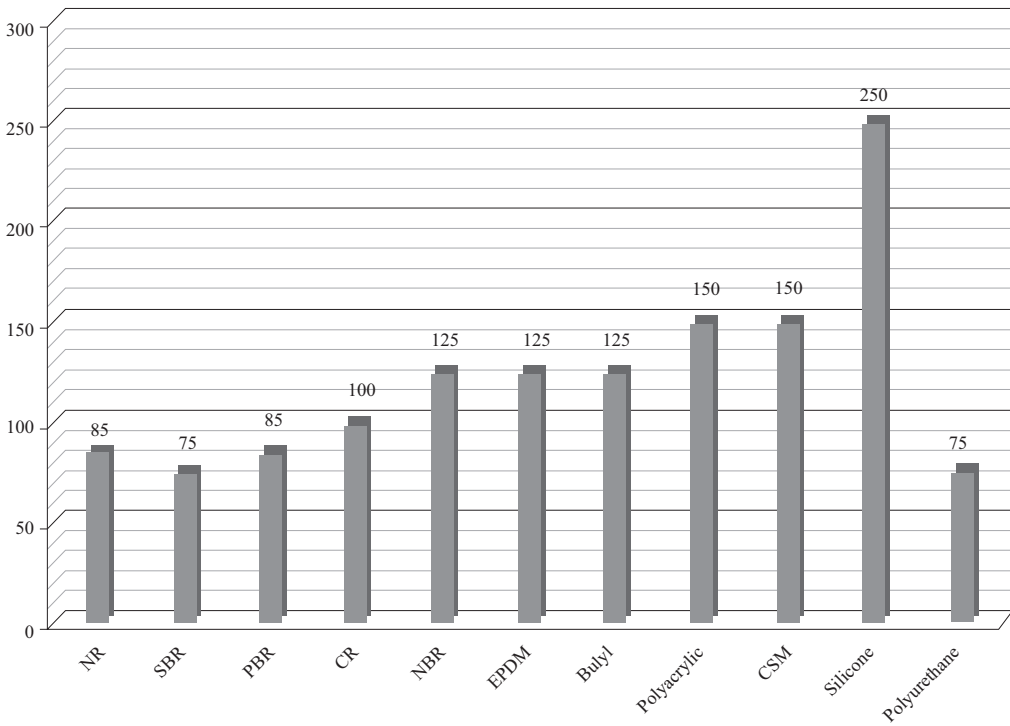


Figure 5.22 Temperature resistance of different rubbers (°C)

The neutral colour silicone rubber composition described previously can be made as a dough in a solvent blends of toluene and xylene. Bonding agent-treated glass fabric can then be coated in a spreading machine; solid content should be maintained at 35%. Thinner coatings of 15% solid content can also be applied for better penetration.

In such cases, multiple coatings are necessary to obtain the specific thickness. This method enhances properties such as strength and flexing. Composites can withstand a service temperature of 315 °C [23].

#### **5.12.4 Sponge Rubber Coating**

The sponge rubber coating usually on cotton fabric is widely used in footwear as inner liner of uppers, and as insole application. Rubber sponge coated on higher thickness durable textiles are also utilised in the making of gaskets for engineering and automobile uses. White textile coated with rubber sponge is exclusively used for sports shoes insoles to offer comfort to the wearer.

A formulation based on natural rubber and SBR blends sponge coating by calendering process is given in **Table 5.15**.

<b>Table 5.15 Sponge coating on cotton canvas for rubber footwear insoles (white)</b>	
<b>Ingredient</b>	<b>Calender coating (phr)</b>
Natural rubber	80.00
SBR-1502	20.00
Renacit-VII	0.50
Titanium dioxide	5.00
Wood rosin	3.00
Zinc oxide	5.00
Stearic acid	5.00
Petroleum jelly	6.00
Precipitated calcium carbonate	20.00
White China clay	40.00
Antioxidant MB	1.50
Aromatic process oil	10.00
Dinitrosopentamethylene tetramine - blowing agent	4.00
MBTS	1.20
Sulfur	2.50
Cure: 2 h at 2.5 kg/cm <sup>2</sup> steam pressure in a steam vulcaniser in roll form	

### 5.12.5 Latex Carpet Backing

The technique of preparing a compound using rubber latex as base material is different from the method of dry-rubber technology of compounding. In latex compounding system the powdery ingredients are essentially dispersed in soft water using a ball-mill, before being added to the basic latex. Similarly, the liquid additives are also emulsified in soft water at an appropriate level.

The dispersed ingredients then added to the centrifuged latex and the mix is then stirred adequately using a mechanical stirrer to finally prepare the latex mix.

An example of a latex composition for carpet backing is illustrated in Table 5.16.

Table 5.16 Latex carpet backing	
Ingredient	Parts by weight
60% Natural rubber latex	167.0
20% Potassium oleate	20.0
20% Ethylene oxide fatty alcohol	5.0
50% Sulfur dispersion	3.0
50% Zinc diethyl dithiocarbamate dispersion	2.0
50% Zinc mercaptobenzothiazole dispersion	1.0
50% Zinc oxide dispersion	6.0
50% China clay dispersion	100.0
20% Styrenated phenol emulsion	2.0
50% Pigment dispersion	3.0
Soft water	Added to adjust viscosity
Cure: in hot air at 120 °C for 30 minutes	

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# 6 Some Applications of Polymer-Coated Textiles and Fabrics

**Bireswar Banerjee**

## 6.1 Introduction

Rubber-coated fabric was made and patented by Charles Macintosh in 1922; it has since evolved into the diverse forms in use today, such as floating bridges, fuel containers, life-jackets, and devices with applications in the fields of aerospace and medicine.

The first inflatable life-preserver was invented by Peter Markus in 1928. It was patented in the USA and improvements were carried out by him in 1930-1931. This life-preserver (which is the present-day life jacket) was extensively used by various air forces during the Second World War.

The British naval officer Lieutenant Peter Halkett first developed two types of inflatable boats intended for use by Arctic explorers in 1844-1845 using rubber-impregnated 'Mackintosh' cloth. The first inflatable pontoons were tested by the Duke of Wellington in 1839.

Inflatable boats became invaluable during the Second World War. They saved the lives of many airmen forced to land their aircraft in the sea. A powered version, the 'Zodiac' is in use today by the military, and as a pleasure craft or inshore lifeboat.

In 1941, a team led by Wilbur R. Franks at the University of Toronto (Toronto, Canada) developed the first 'G-suit', which was filled with water. American pilots tested them during 1944, but found the water system uncomfortable, so air-inflatable designs were developed.

Air-inflatable G-suits were very common in North Atlantic Treaty Organisation (NATO) aircraft of all nations from the 1950s onwards and are still in common use today. They allow pilots to safely fly under high accelerations.

## **6.2 Domestic Applications of Rubber-coated Textiles**

### **6.2.1 Rainwear, Cycle Jackets, and Wind Cheaters**

Protective clothing such as raincoats and cycle jackets are designed for use as outer garments. They are fabricated from rubberised textiles made of natural fibres, man-made fibres, or a blend of the two. The making of these items starts from cutting coated fabrics, subsequent stitching, and the fixing of buttons and zip fasteners. The vulcanised rubber coated fabrics are cut into long pieces, and laid 16–18 layers in plies. The top layer is marked with coloured chalk with the help of perforated templates made according to the design of the components of a garment. A cutting machine is then used to provide the desired shapes.

The cut components are inspected and matched according to their colour shades, and subsequently stitched at 8–10 stitches per 2.5 cm length. Stitching operations are done by motorised sewing machines to make a complete raincoat. The making of button holes, fixing of buttons or fixing plastic zip fasteners are then done to complete the garment.

To seal the pinholes along the stitching lines, rubberised fabric tape of desired width is cut into a bias angle, and placed on the seams by hand at the inner part of the stitched raincoat/jacket and trouser. Seam lines are coated with room temperature cured rubber adhesive before ‘taping’ with a small hairbrush. This taping is done along the stitching line to prevent the garment being penetrated by rain drops. Raw uncompounded natural rubber latex can also be applied by a hairbrush along the stitching pinholes before applying the tape to make more secure sealing of the minute holes caused during stitching. When dried, the latex layer prevents water penetration through the pores.

After completion of the taping, the coat is cleaned with the help of solvents. The rubber-coated surface of the fabric can be polished with the help of a silicone emulsion in water. Finally the garment is packed according to the dimension/size tag provided in each coat.

In general, in lighter varieties of raincoats, the rubber-coated surface of the fabric is put on the outside, and the uncoated fabric surface is on the ‘body’ side to allow adequate ventilation. Some are designed with an uncoated fabric outer and the coating layer on the body side to make the garment more fashionable with coloured or printed designs on the outer surface.

Rainwear made for women and children is fabricated from brightly coloured or printed textiles of single-textured (ST) coated fabric, and less bright shades are used

for men's raincoats. For raincoats which are used by security personnel, woven drab (khaki)-coloured double-textured (DT) fabrics are utilised. They are prepared using the rubber coating in-between the two fabric layers, and provide high durability. Many other colour shade fabrics are also used for making this variety of raincoats.

To make the rainwear highly durable, suitable for rugged use, and to provide a long service life, the coated textile is made from DT fabric (e.g., rainwear for military use) instead of using a ST fabric. A DT raincoat with arm vents for ventilation is shown in **Figure 6.1**.

A DT fabric for rainwear is made using a thinly coated inner liner of plain or printed design fabric with rubber solution on one side in a spreading machine, and the coated surface is pressed together on the rubber-coated surface of another coated fabric duly coated in the calender machine. The doubled fabric is wound up at the other end of the machine. The equipment used for making DT fabric comprises a rubber-coated roll on a metallic roll which revolves at a specified speed. Pressure is applied on the rubber roll by weight or by a pneumatic device to give adequate pressure which firmly adheres the two layers of fabric. It forms a doubling of the two coated layers of fabrics. The composite is then vulcanised in an autoclave in roll form. After curing the DT-coated textile is tailored for making raingear [1] (**Figure 6.1**).

The selection of the proofing process by a wet system in spreading or by a dry system in a calender machine is dependent upon fabric weight as well as the coating weight of the rubber compound to be applied. Lighter varieties of fabrics (natural or man-made) weighing  $<60 \text{ g/m}^2$  can be coated by the solution coating method in a spreading machine to avoid damage to the fabric due to calender roll pressure.

Fabrics above this weight can be coated with dry rubber mixes in a calender machine. The choice of coating process is also dependent upon the quantity of coating to be applied on the fabric. A proofing weight of  $\geq 120 \text{ g/m}^2$  is recommended for coating in a calender machine, whereas material below this weight is processed in a wet system by a spreading machine.

A quantity of  $7\text{-}10 \text{ g/m}^2$  can be deposited by each pass at a speed of  $12\text{-}15 \text{ m/min}$  in knife-on-roll equipment. The solvent is evaporated by passing over steam heated chests immediately after coating, wound up on rolls, and kept ready for subsequent coating. Higher coating thicknesses are obtainable on increasing the number of passes.

A coating thickness of  $0.125\text{-}0.15 \text{ mm}$  per pass and a proofing weight of  $150\text{-}180 \text{ g/m}^2$  can be obtained by the dry method in a calendering system. Care needs to be taken to obtain a thickness of coating if operating the machine at a higher roll temperature.





a)



b)



c)



d)

**Figure 6.1** a) Rubberised raincoat; b) Nylon rain jacket; c) German army poncho (reproduced with permission from Surplus and Adventure, Worcester, UK); d) double texture rubberised raincoat with arm vents

The woven fabric employed for proofing and making raincoats/cycle jackets is primarily cotton plain weave, lightweight Nylon and polyester, or blends of synthetic fibres with cotton. Rayon blended with cotton in attractive colours gives a 'silky' look and offers aesthetic value to the finished garment. It can be used for producing rainwear for ladies and children.

Windcheaters are fabricated from bright and attractively coloured, synthetic lightweight fabric coated on one surface of fabric with a very thin layer of rubber mixes in matching shades. Natural rubber (NR) and blends of NR/styrene-butadiene-rubber (SBR) proofing are suitable if a thin coating is applied on the treated synthetic fabrics for improved adhesion.

Certain grades of polyacrylic rubbers (ethyl acrylate type) can be readily dissolved in solvents such as acetone/methyl ethyl ketone without being milled, and a very thin coating of the solution can be spread on the fabric. A small dose of polyisocyanate (Desmodur RF) is added to the solution as a curing agent at room temperature after drying by passing over the steam chest. Conventional vulcanisation is avoided by following this system of coating. This polymer remains flexible in the low temperature region of  $-40^{\circ}\text{C}$  if the garment is used in high-altitude snowbound areas.

In the making of wind cheaters, coatings of polyurethane (PU) polymer on synthetic textiles are also used. PU coatings can be applied on to the fabric as a single-component system or two-component system. A very thin layer of coating ( $20\text{--}40\text{ g/m}^2$ ) may be applied on the fabric using this elastomer in a specially designed spreading machine.

The proofed fabric is cut according to the specified design and tailored. Headgear of a suitable design is incorporated and put into a folded form in the pocket provided on the collar of the jacket with a plastic zip fastener. The whole windcheater can be folded and packed in a small pouch made from a similar fabric (uncoated) for convenience.

Rubber-coated fabrics are tailored to make ponchos, which are used by the military especially in mountainous terrains. This personal protective gear used as a raincoat can also be used as a groundsheet for sleeping, and can be utilised as a field shelter. Ponchos could be combined to make a two-person tent and may serve as a raincoat or as an individual shelter. This gear is also used by hunters, campers, and rescue workers. To make a poncho into a tent, two 1.5-2.5 m ropes, six sharpened sticks ( $\sim 30\text{ cm}$  long) and two trees 2-3 m apart for tightly stretching the poncho are needed.

A rain proof poncho is made from a large waterproof coated fabric sheet. Rubber-coated Nylon rip-stop fabric is tailored to fabricate a rain poncho, which is an important piece of kit for military personnel because of its multiple use (blanket, sleeping bag, groundsheet). It should be lighter in weight, and designed so that it not only covers the wearer but also the wearer's pack. Ponchos are available in various

colours (e.g., black, olive green). Lightweight coated Nylon and other synthetic fabrics have been developed to make military ponchos [2] (Figure 6.1).

#### **6.2.1.1 Polymer-coated Breathable Fabrics**

Elastomeric coating membranes on textile fabric are used mostly in protective apparel to impart waterproofing and wind resistance. However, making fabrics waterproof as well as breathable to provide adequate comfort to the wearer is difficult.

Breathable proofed fabrics allow body moisture to pass through but do not allow raindrop particles to penetrate. This gives comfort to the user. They are useful mostly in tropical and subtropical regions.

The breathability of a textile-polymeric composite can be defined as the ability of the material to allow moisture vapour to permeate through it, but without allowing rain, wind and other liquids to pass into it. This process allows human perspiration water vapour which accumulates under the polymer barrier to be carried away from the skin surface. It is expressed as the 'moisture vapour transmission rate' (MVTR). The MVTR is measured at a unit area in unit time in  $\text{g/m}^2/\text{h}$ . Breathability is an important criterion for a coated textile if used as a barrier to air and liquids simultaneously, providing a 'comfort factor' to the user. Water vapour transmitted by the body due to perspiration can permeate through the fabric to the outside to provide increased comfort. This level can be maintained at a MVTR of  $\sim 2500 \text{ g/m}^2/24 \text{ h}$ .

This property of breathability is not only important for the proofed textiles used in garments, footwear, aprons, and clothing for medical purposes, but is also necessary at a faster rate for use in making tents, domes, and even in producing waterproof roofing membranes.

A very thin coating of a specific type of PU can prevent wetting from body oils to the laminate, and can allow wicking of moisture through the membrane. This material (or a composite) provides protection to the wearer and also helps to transmit sweat evaporation from the body. In contrast, conventional rubber-coated rainwear which does not feature this mechanism of breathability results in accumulation of moisture vapour on the body side of the coat/jacket, and does not allow sweat to evaporate effectively, giving discomfort to the wearer.

By application of the 'wet coagulation' method, a microporous layer of waterproof, moisture-permeable coated fabric can be produced using a coated solution containing a polar organic solvent, PU elastomers, a water repellent agent, a polyisocyanate, and a non-ionic surfactant.

Deposition of a microporous layer should be  $\leq 33\%$  of the total thickness of the substrate fabric. In general, the higher the coating the more waterproof and windproof it is. However, a thicker coating gives increasing resistance to permeability of moisture vapour, and the minimum necessary peel strength should be 100 g/cm.

The microporous PU membranes designed for internal layers of textile-polymer composite systems have a coating weight of 40 g/m<sup>2</sup> and a thickness of 50  $\mu\text{m}$ ; no percolation of water occurs when a 250 cm water column is used for testing. At the same time rate of permeability of water vapour and under static conditions of  $\sim 2000$  g/m<sup>2</sup>/24 h can be effectively used for making clothing.

To provide adequate comfort for the wearer with such protective garments, some coated materials in which access to the breathability mechanism without allowing rain or wind to penetrate from outside have been developed. One such material bears the trade name Gore-Tex. It is a porous form of polytetrafluoroethylene (PTFE) with a microstructure characterised by nodes interconnected by fibrils. It has a composition of a thin porous fluoropolymer membrane with a urethane coating, and is bonded to a fabric such as Nylon or polyester.

The membrane consists of  $\sim 1.4$  billion pores/cm<sup>2</sup> (which are several thousand times smaller than a rain drop). Hence, water droplets cannot penetrate through these minute pores, but they allow moisture vapour from the body to pass through: the material exhibits breathability. This material can also be used for making windproof jackets and has breathability.

Application of Gore-Tex in making tents for recreation, expedition and educational purposes in remote areas has been found to be highly effective [3].

A novel development in producing breathable elastomer-coated fabrics is described in a US patent (Heeter and Lawrentz 1994) granted for a processing method of a coating system. As claimed by the inventors, natural or man-made fibres or their blends in woven/non-woven textiles can be coated with the polymers such as NR, SBR, acrylonitrile-butadiene rubber (NBR), polychloroprene (CR), ethylene-propylene-diene terpolymer (EPDM), butyl rubber, PU, polyvinyl chloride (PVC) or their blends.

The proofing process of the fabric substrate is undertaken with the elastomeric latex on the top surface in the horizontal position. A flow of hot air is applied through the bottom surface using one or more knives. The latter are in direct contact with the bottom surface of the substrate, creating pores in the polymeric matrix on the top.

This system of proofing can produce breathable polymeric-coated fabric consisting of multiple microscopic pores. The latex is foamed before applying and a gelling agent

added to the latex. This can be considered to be an important invention in the field of breathable coated-fabrics, and has tremendous commercial scope. Further technical information about the manufacturing systems has yet to be released

Another invention in this field was made by Schortmann in 1994 and patented in the USA. It involved the production of a non-porous breathable barrier fabric. Sizing a textile fabric woven/non-woven fabric with a film forming clay-latex filler material provides a high-strength fabric that is permeable to water vapour but impermeable to air and aqueous liquids.

The breathable barrier fabric film forming clay-latex filler material is an aqueous clay-latex formulation that permits diffusion of water vapour.

The MVTR is claimed to be 300–3,000 g/m/day. This coated material is also claimed to be a barrier against wind, dust or other airborne contaminants such as pesticides, bacteria, and viruses.

For the last three decades the thermoplastic polyurethane (TPU) has been used in textile–polymer composite systems. The unique properties of abrasion resistance, toughness, chemical, hydrolysis resistance, and fungal resistance, along with low temperature flexibility and colourability, enable its uses in a range of coated textiles. It has excellent drape properties, softness, and can be processed to high surface gloss, suitable for producing protective clothing and sportswear.

Its properties of leather-like feel have led to use in coated textiles for footwear applications. Polyether-type breathable TPU has been developed and is commercially available (Estane made by Noveon) having five to six times more MVTR. The film of extruded TPU can be laminated onto a textile substrate which acts as highly breathable barrier, allows moisture vapour to escape out from the body surface, and simultaneously prevents liquids penetrating. It can give comfort between the user and the environment, and simultaneously work as an effective barrier.

Due to these specific properties, this particular TPU can be used in textile polymer composite systems for producing protective and medical clothing, and sportswear. Photographs of breathable waterproof jackets and boots are shown in **Figure 6.2**.

#### **6.2.1.2 Permeability and Impermeability Factors of Coating**

The property of breathability is different to the phenomenon of permeability. This is because many of the fibres used for making textiles absorb moisture from the atmosphere, and the rate of absorption is dependent upon the humidity of the environment.

Liquids and vapours permeate through the rubber membrane by dissolution in the elastomers, and diffuse through the polymer barrier. Permeability depends on the physical and chemical composition of the polymer. The permeability of gas decreases with increasing density of elastomer crosslinking. The permeation rate of gases, liquid and vapours varies with the pressure differential which initiates the permeation, and is also related to the thickness of the polymer barrier.

Elastomers such as NR, SBR, and EPDM rubber exhibit poor gas and vapour permeability. Butyl rubber shows very high resistance to permeation of air and gases, epichlorohydrin rubbers have extremely low permeability to gases of about one-third that of butyl rubber. A highly permeable elastomer is silicone rubber.

This property is beneficial to some of the special application areas such as devices for medical uses. Polymers having high permeability are used in the production of oxygen-permeable diaphragms.

Thin films of silicone rubbers selectively permeable to different gases are used for separating gases to obtain relative enrichment of one gaseous component over another. A thin film of dimethyl silicone membrane of 25  $\mu\text{m}$  thickness permeates 50 litres of oxygen/ $\text{m}^2$  at a pressure difference of 0.1 MPa.

Many textile fibres regain moisture from the atmosphere, and this is higher if the moisture content of the surroundings is high. The percentage of moisture absorption is higher in natural and Rayon fibre (8% and 13%, respectively). It is lower for synthetic fibres.

Chemical compositions in liquid form applied to the outer fabric surface of rubber-coated rainwear as water repellent treatment will repel rainwater droplets and prevent the fabrics from absorbing water. Proprietary sprays are also available which can be applied at intervals to maintain the water repellency property, but these are not permanent.

In the application of making protective garments, water repellency can be achieved by applying water repellent treatments on the outer surface of the fabric. It may provide comfort to the wearer because the moisture vapour from the body will evaporate out from the porosity of the treated fabric. This type of treatment on the fabric is not permanent, and can be removed during cleaning of the garment. The fluoropolymer base sprays (Scotchguard) can be applied as water repellent agents. This again requires re-application because it may be rendered ineffective after a few washes [3].

Protection for longer duration can be provided by elastomeric coatings on one surface of a fabric that can be defended from rain and wind. However, the impermeable,

continuous layer under which body vapour accumulates is uncomfortable for the user, and this problem is severe in humid tropical regions.



**Figure 6.2** Breathable rain jackets and boot with breathable upper

### **6.2.2 Latex Coating on Fibre and Textiles**

NR and synthetic rubbers in latex form are also used for coating fibres and textiles. The techniques applied to coat woven/non-woven fibres are dipping, spreading or spraying. On drying of the compounded latex by applying heat, a film of rubber is formed on the fabric surface.

SBR, CR and nitrile rubber synthetic latices can be compounded alone or blended with NR latex for use in coating applications. The solid content of these latexes should be 50–60% to obtain a good coating of film. In CR for flame-retardant applications, and for oil-resistance uses, nitrile rubber lattices can be selected. These may also withstand the dry cleaning of the coated material.

The widest application of latex coating is in carpet backing to anchor the piles, and to simplify the weaving structure. This provides a very good non-slip property for the carpet. Carpet back coating can be done using latex foam mixes to get a non-slip finish.

Spraying with foam latex compound on coir fibres from vegetable origin or animal hair can be used to make mattresses/upholstery for beds, sofas, and car seats. Curing of these articles can be conducted in steam coil-heated air ovens without pressure. Drying and duration of vulcanisation of the latex coating are dependent upon the thickness of the coating [4]. A nitrile rubber latex coating on cotton knitted hand gloves is depicted in **Figure 6.3**.



**Figure 6.3** Nitrile rubber gloves (latex dipped)

### **6.2.3 Hospital Sheeting, Bedspreads, Baby Mats and Aprons**

Rubberised hospital sheetings are generally coated with NR alone or a blend of SBR/ NR on both sides using lightweight cotton/polyester or blend of cotton polyester



fabrics as substrate in the colour range of white, red, brown, blue or green. The total thickness of the sheeting should be 0.35-0.4 mm and the breaking strength of a 5 × 20 cm strip will be 25 kg/min. It should be highly flexible and sterilisable in an autoclave for at least for 8-10 times. Sheets and covers of this type are used in hospitals [5].

Baby mats are proofed on both sides on lightweight pure cotton, cotton/synthetic blends or on Nylon fabric with a blend of NR or NR and SBR coloured compounds.

The long length coated fabric is cut in sizes of 1 × 2 m and packed in printed plastic bags for the market. Careful selection of the compounding ingredients with reference to the toxicity of the rubber chemicals is important in formulating baby mats, providing mixes that should not affect the baby's tender skin [6].

#### **6.2.3.1 Rubber-coated Textile Aprons**

Rubber aprons for use in abattoirs are coated on both sides usually on cotton fabric in white/light-brown/black colours. The total thickness should be 0.60–0.65 mm. NR or blends of NR/SBR-coated textiles should be able to withstand sterilisation processes at 120 °C for at least 8-10 cycles.

A neck support strap and a pair of waistbelts are provided for fastening. Because of the heaviness of cotton-coated aprons, Nylon fabric thinly coated with CR by solution spreading can be used and withstands many sterilisation cycles.

Aprons for vegetable oil/petroleum oil processing industries use the oil-resistant nitrile rubber alone or in blends with NR or SBR for coating on cotton or textiles of natural/synthetic blends. Thickness should be maintained at 0.3-0.35 mm, and this can give the higher breaking and tear strength necessary for industrial purposes. For flame-resistant applications, CR with flame-proofing additives using cotton fabric as the substrate gives satisfactory service. These may also be suitable for domestic uses [7]. Photographs of CR-coated apron and different coloured aprons for abattoirs are shown in **Figure 6.4**.



**Figure 6.4** Rubber coated aprons for industrial use (both sides are coated)

#### **6.2.3.2 Ice Bags**

A pouch type, conical shaped 15–20 cm long rubberised bag, fitted with a round top plastic screw cap can be made from Nylon fabric or Nylon/cotton blended fabric coated on one side with NR, NR/SBR. The rubber coating is on the inner side - these are used to make ice bags used for cold therapy. They provide first-aid treatment with ice/cold water particularly for sports persons for any injury, swelling or trauma. Ice bags are most useful as an aid to bring down high body temperatures. A pouch-type ice bag with a plastic cap is shown in **Figure 6.5**.



**Figure 6.5** Rubberised fabric ice bag

#### **6.2.4 Coated Textiles in Footwear Applications**

Different types of rubberised fabrics (including natural fibres, cotton, man-made textiles or blends of these) which are woven or non-woven in various colours, textures and strengths are made for the footwear industry as uppers, inner liners, or toe caps. Rubber-coated textiles are used for making the uppers of footwear for use in domestic, industrial, defence and sports shoes on rubber/PVC/ethylene-vinyl acetate copolymers or thermoplastic polymer soles.

Textiles coated on one surface (ST) are used as reinforcing members on the inner lining of leather/cotton canvas/synthetic uppers by adhering the rubberised surface to the inner surface of the upper using suitable adhesives. In some footwear, flannel or raised synthetic pile fabrics, thinly coated with rubber solution on the woven plain side, are fabricated as the inner liner for the rubber shoes used in snowbound areas to give warmth to the user (e.g., snow ankle boots). In leather/synthetic upper shoes, coated textile lining is used by adhering with self-cured rubber-based adhesive to provide sweat absorption to the footwear.

Cut from the long length, vulcanised DT rubberised fabric in a punching machine, the components are stitched in the shape and design of the uppers as per the size matching to the shoe. They are assembled by hand with uncured calendered, suitably designed soles and moulded heel part on metallic lasts. Subsequently, the whole shoe is vulcanised in an autoclave in batches. The soles can also be compression/injection moulded on the rubber-coated textile uppers.

DT rubberised fabric uppers offer adequate strength and provide shape retention to the shoe during the service life.

The factors to be considered for the selection of a woven fabric in the application of footwear are (i) type of fibre, (ii) construction of the fabric, and (iii) requirement of physical properties.

The desirable basic properties of elastomer-coated textile uppers for rubber footwear are:

- High waterproof nature of the upper.
- Retention of shape and design (dependent upon the weight, texture and rubberisation of the fabric).
- High adhesion strength between the plies for DT fabrics.
- Good flexibility (provided by good design of the rubber compound for coating).
- High colour fastness of the textile. This depends on the process and type of colouring matter used in dyeing the fibre (natural or man-made).

Rubber-coated fabrics to be used in making different categories of footwear should be optimised for offering strength, modulus, abrasion resistance, and resistance to bacterial attack.

In producing highly waterproof rubber footwear (e.g., gum boots), coated fabric is used as the reinforcing membrane as the inner liner and the outer part is lined with rubber calendered sheets. These types of footwear can be produced by hand on metallic lasts or by compression moulding.

An important area of application of rubberised fabric in footwear component manufacture is toecaps, which protect the wearer of the shoe from scuffing/injury, and also help to emit body vapour from the toe area. The material required to be used is rubberised strong cotton lined with a non-woven textile. Coating can be done with NR mixes or blends of SBR/polybutadiene rubber (PBR) with NR should give flexibility and the desired adhesion.

Rubber sponge 'insoles' are lined with rubber-based sponge compounds, calendered on twill/drill weave fabric cotton, vulcanised in roll form in an autoclave, and punched out in the desired sizes. In sports shoes, a higher thickness sponge insole is used if a shock-absorbing effect and comfort are needed.

These rubber-lined fabric insoles can be used in all categories of footwear (including PVC and leather boots). A minimum thickness of 2 mm provides comfort for the wearer.

High breaking and tear strength DT rubberised fabric is employed for producing 'safety footwear' uppers. These are used in miners' safety boots with steel toecaps, jungle boots for military and expeditions, and in footwear for heavy industries. The fabric chosen is cotton canvas/man-made fibres or blends of synthetic and natural fibres to achieve the desired properties of high strength and high tear resistance.

In industrial footwear uppers, the 'leno' weave fabrics are preferred to provide a very stable structure. Their weave construction gives strength advantages (warp threads cross each other, thereby locking the filling thread). To absorb sweat from feet, the inner liner of such DT fabric of  $2 \times 2$  cotton twill weave will be adequate.

This particular weaving pattern of fabric provides very high tear strength, and also imparts improved cut resistance to the shoe uppers. The heavy weft yarns can act as a 'ripstop' (i.e., to prevent tear propagation if the shoe upper is cut by sharp objects) when used in mines and heavy industries. Proofing by NR or blends of NR and general purpose synthetic elastomers provide desired flexibility, high waterproofing features, and durability.

The minimum breaking strength of ripstop fabric used for the over layer of the upper for industrial rubber-proofed canvas boots should be 168 kg ( $5 \times 20$  cm test piece) in the warp direction of the fabric and 137 kg in the weft direction. The breaking strength of the cotton inner liner should be 102 kg in the warp direction and 56 kg in the weft direction. The adhesion strength on rubberisation of the DT fabric used in making boots should be  $\sim 4$  kg/cm.

For use in oil processing industries, the coating should be based on CR or nitrile rubber or its blends to impart adequate oil resistance and adhesion strength to the DT textiles converted in making the uppers of the boots.

In high-risk industrial uses for protection against powered saws, the 'vamp' portion (metatarsal part of the foot) of the footwear may be fabricated with high cut resistance, excellent tensile strength Kevlar (aromatic polyamide) fabric. The DT rubberisation may be made with this fabric using an under layer of cotton fabric.

Fire fighting boots similar in design to the gum boot but with the inclusion of flame-resistant rubber on the outer layer may be compounded from CR incorporating flame-retardant ingredients in the mixes.

The inner lined fabric may be treated with a flame-retardant liquid, and then coated with rubber solution on cotton fabric in a spreading machine. The calendered outer sheet is laid on the textile liner with the help of a rubber adhesive or simply wiped with solvent to develop adhesion, to make a composite for assembling into a boot. On completion of the assembly operation by hand on an aluminium last, the boot is vulcanised in an autoclave in batches.

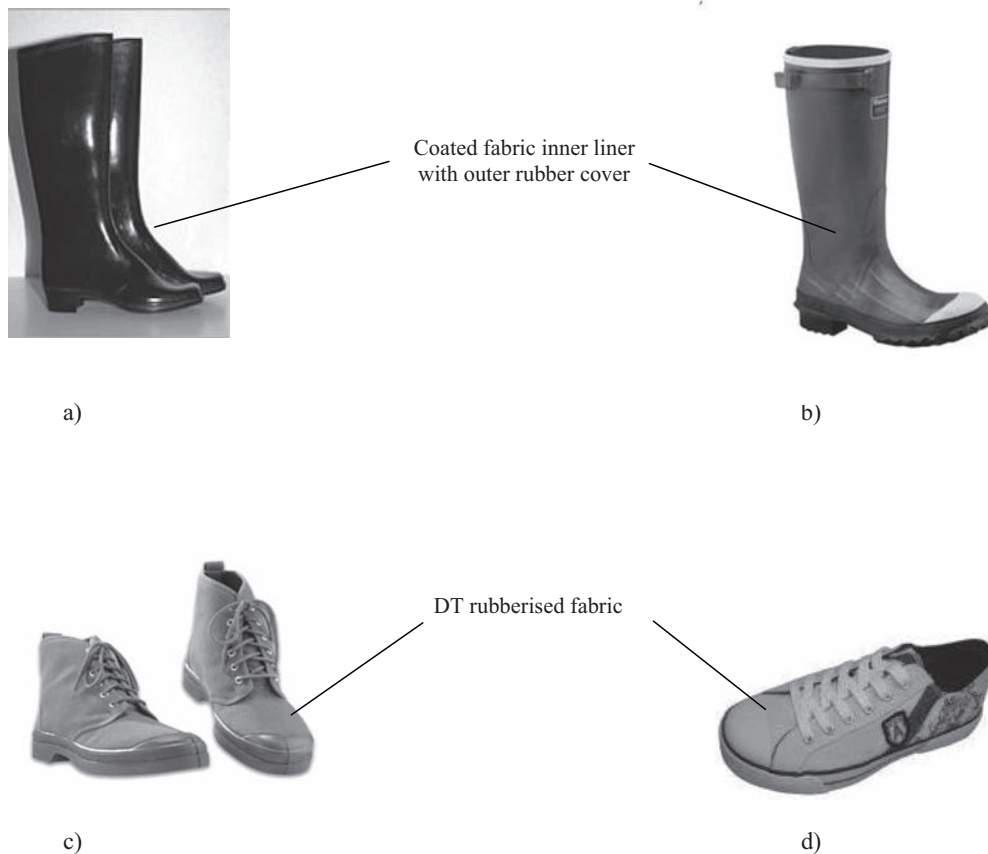
Cold weather footwear as used by the military and by mountaineers has a outer made from all rubber sheeting (usually white in colour). The inner liner is fabricated with highly insulated acrylic pile fabric. The liner's plain surface is coated with rubber solution to adhere to the all-rubber sheeting which forms the outer layer. The total assembly is then vulcanised in an autoclave.

Sports shoes are the most versatile application of rubber footwear. They have an upper constructed from rubberised textiles of special texture and design for athletes, tennis players, basketball players, and for physical exercise. Construction of this category of shoes should be lightweight, with a cushioned upper with a soft inner liner to offer highly comfortable wear without fatigue to the wearer. They are usually hand-fabricated on rubber, PU or thermoplastic elastomer soles and heels, but can also be injection/compression moulded with coated textile uppers.

Durability for high performance athletic shoes depends upon correct design, and selection of basic materials and components. Rubberised DT fabric (usually white in colour) made from cotton or synthetic fabric or their blends offers high flexibility, comfort and durability to the user. A rubber sponge coating on twill/drill weave cotton fabric is punched as per the size of the finished shoe and inserted as the insole [5]. Photographs of various shoes and boots are shown in **Figure 6.6**.

### **6.3 Rubber-coated Textiles for Producing Industrial and Automobile Products**

Applications for rubber-coated textiles in waterproofing, air/gas proofing, and chemical proofing in the engineering and industrial fields are extensive. For defence purposes, the design engineering aspect and requirement for specific performance are important in the selection of the correct type of coated fabric for ultimate product functionality.



**Figure 6.6** Different types of rubberised canvas footwear: a) black rubber gum boot; b) rubber industrial gumboot with steel toe caps (reproduced with permission from La Crosse Footwear Inc, Portland, USA); c) rubberised canvas jungle boot; d) rubberised canvas tennis shoe

Various types of rubber hoses for conveying air, gases, water, fuels and hygienic materials are used in distilleries and soft drinks plants where rubber-coated textiles of man-made or natural fibres in different weaves, structure, and strengths are utilised as reinforcing members. Elastomers employed for coatings in these products are NR or blends of general purpose synthetic rubbers, NBR, CR, silicone and chlorosulfonated polyethylene (CSM).

### **6.3.1 Insertion Sheets, Diaphragms and Gaskets**

For these purposes, both side-coated cotton, synthetic textiles and, in some applications, glass fibre cloths, are coated with oil-resistant NBR/CR or polysulfide rubbers to get high oil- and heat-resistance components to be used in automobile or engineering applications.

Ground sheets and tarpaulins can be fabricated from DT cotton or a combination of cotton/man-made fabric coated with NR/EPDM/CR/CSM. Ground sheets used as flooring camping and tarpaulins should be of high water-, weather-, and sunlight-resistance, as should those used for tents, covers for trucks and engineering installations.

Rubber-coated jute textiles (the latter a natural fibre and biodegradable) can be deployed for several domestic and industrial purposes.

### **6.3.2 Hoses**

There are types of fibres woven, knitted and cords from natural, man-made and/or mineral origin which are utilised to reinforce the carcass of different types of rubber hoses. To acquire the optimum service performance of a hose, it is imperative that the coated textile cover of the hose is fully consolidated and bonded together with the rubber inner tube.

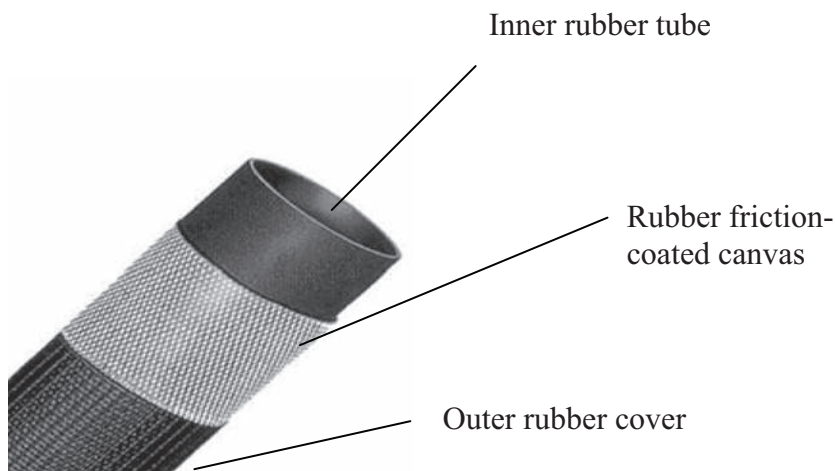
Mineral fibres such as asbestos and glass in woven form are rubberised and applied over the inner rubber tube to construct a hose for high heat-resistance applications.

Cotton textiles of different breaking strengths depending upon the burst pressure of the completed hose are coated with elastomeric compounds, and are used as the reinforcing member. The woven fabric or cords may be coated in a calender machine to a desired thickness of coating on the substrate. In support of improved adhesion with the subsequent coating in a calender, a primary base coating of rubber solution in the spreading machine (or for the higher weight fabric a friction coating of the textile in a calender) is essential to get the desired adhesion with the subsequent coating in a calender machine. Steel wires/cords are applied as reinforcing members in high-pressure hoses over the inner rubber tube. In this case, a rubber layer is essential on the steel wire, and the latter should be treated with a bonding agent for adhesion with the rubber coating.

For the purpose of water delivery and suction hoses, NR or blends with general purpose synthetic elastomers are applied to coat the textiles. In oil-resistant hoses,



the fabric should be coated with CR or nitrile rubber mixes to obtain adequate oil resistance [8]. A cut section of a typical rubber hose is shown in **Figure 6.7**.



**Figure 6.7** Rubber hose used for water delivery. Reproduced with permission from Kuber Rubber Industries Delhi, India

### **6.3.3 Conveyor and Transmission Belting**

Rubber conveyor and other transmission beltings (i.e., flat belt, vee belt) are reinforced with rubber-coated textiles, cords or steel cords in constructing their carcass to protect the belts from damage by impact in continuous mechanical action.

Conveyor belts are fabricated by laminating several rubber-coated textiles in plies. They are then consolidated, and finally the constructed raw belt is vulcanised in long steam heated hydraulic presses or in a rotary curing process (rotocure system). Before the introduction of synthetic fabric, cotton duck (80-200 g/m<sup>2</sup>) was generally used depending on the severity of use of the belt.

To impart improved physical properties to the product, synthetic continuous filament fibres can be used which also considerably reduce cost when compared with natural fibres per unit strength.

In manufacturing processes for different types of belts, Nylon fibre is the major reinforcing agent. Its high strength, low modulus, and high elongation at break in comparison with other man-made fibres (e.g., Rayon and polyester) as well as resistance to damage due to impact, and energy absorption owing to its extensibility are the essential characteristics. These important properties of Nylons make them particularly interesting to belt manufacturers. Modification of extensibility can be done by heat stretching and heat relaxing during belt manufacture.

To improve bond strength with a rubber matrix of continuous filament fibres such as Nylon/polyester fabrics needs special treatment through the use of bonding agents. The technique of treatment of fibres with bonding agents improves the desired adhesion strength with the rubber coating and the textile. This is discussed in detail in **Chapter 5**.

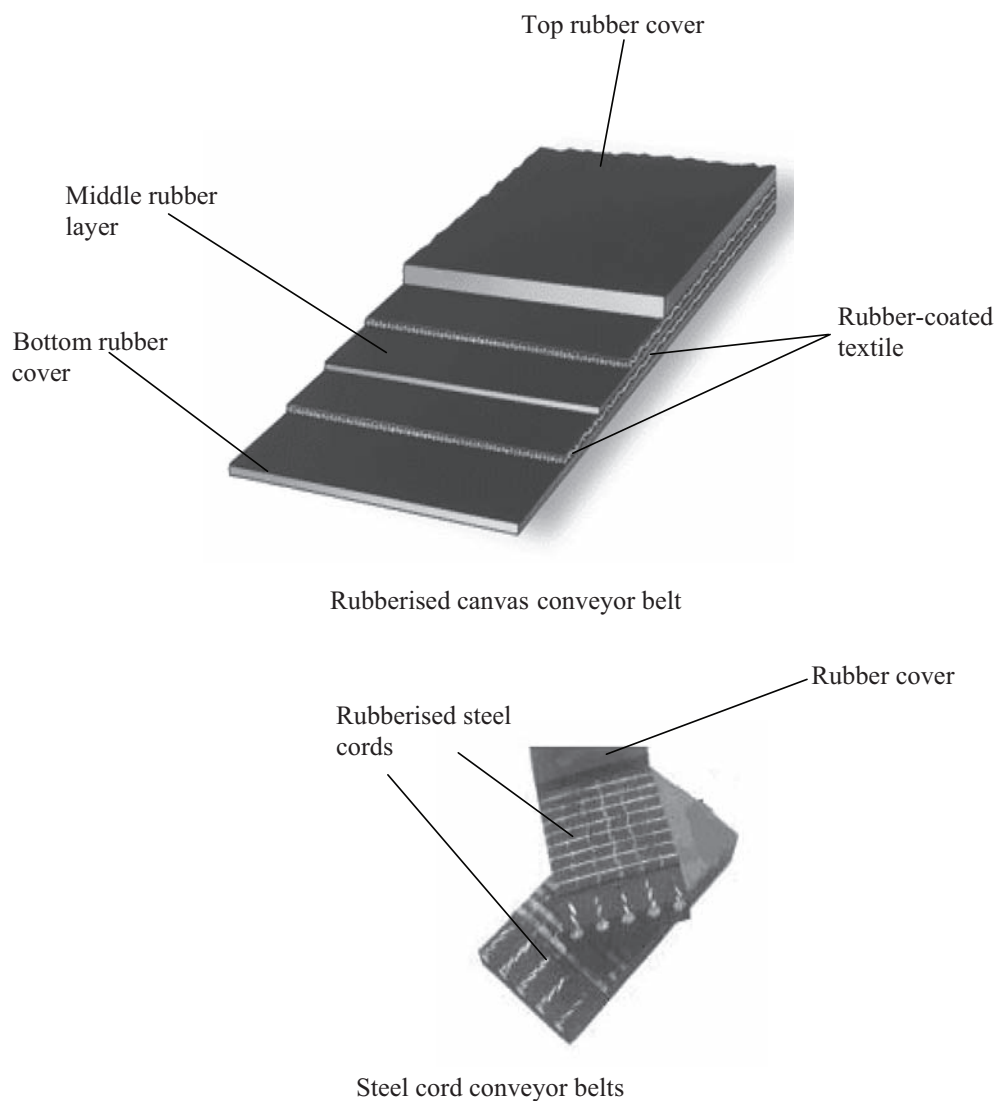
In general, there are four categories of rubber conveyor belts which are produced using rubber-coated textile reinforcement:

- General purpose
- Oil-resistant
- Heat-resistant
- Hygienic or food-grade conveyor belts

The food grade category belts are usually made in a white colour. The toxicity level of the rubber compound must be maintained as to the food safety norms.

Coating of the reinforcing textiles used in belts can be done in a 3/4-roll calender machine. Friction coating on each side of the fabric is necessary to obtain the desired bond strength of the rubber matrix. Cut sections of a textile reinforced conveyor belt and steel cord reinforced belt are illustrated in **Figure 6.8**.

The fabrics designed for belt making are usually friction-coated before the application of a top coating of rubber in a rubber calender machine. However, lightweight fabrics for low strength belts can be solution-coated in a spreading machine before subsequent coating in a calender. In some cases, heavier fabrics are subsequently skim-coated after fractioning.



**Figure 6.8** Cut sections of canvas and steel cord reinforced conveyor belts

In the manufacture of general purpose conveyor belts, NR, and NR/SBR blends are used to coat the textiles and to make cover compounds. EPDM/butyl rubber mixes are utilised for heat-resistant belts, and for oil-resistant applications CR/NBR are the materials of choice.

Careful selection of polymers and compounding ingredients are necessary for hygienic conveyors, NR, SBR, and nitrile rubbers are suitable for use in food-grade products.

Following the process of manufacturing conveyor and flat belts, full-width textile fabrics of specified properties are first calendered for friction coats and skim coating, and subsequently a top coating is applied. The coated fabrics are then cut according to the desired width, and plied together on long building tables or by mechanical means.

Calendered sheeting prepared from all rubber compounds at the desired thickness is placed on the top and bottom of the plied carcass as covers. The completed green belt is then wrapped on a fabric/plastic sheet liner, and stored in roll form. It is then cured in a long steam heated hydraulic press in sections or in a rotocure machine on a continuous curing system. While curing is occurring the in press, the whole belt is stretched at ~8-10% for the elongation remaining from the reinforcement agent.

The textile fabrics which are utilised in the manufacture of conveyor carcass are usually of heavy gauge, and are in the range 750 g/m<sup>2</sup> to 1100 g/m<sup>2</sup> weight. A completely finished belt breaking strength of a three-ply Nylon reinforced belt is ~500 kN/m and for a four-ply belt is ~800 kN/m [9].

#### **6.3.4 Offset Printing Blankets**

One of the most critical industrial applications of rubber coated textiles is in the printing industry for use in offset printing presses in printing paper/textiles.

Good quality cotton fabric specially woven from long fibre cotton or a blend of cotton/Rayon is used as the reinforcing substrate of rubber printing blankets. A weight of fabric substrate of 95-190 g/m<sup>2</sup> with high breaking strength of ~50 kg/cm, very good dimensional stability, and low stretchability (7.5% elongation at break) are the essential requirements for the manufacture of offset printing blankets.

Pretreatment of fabric is necessary to remove stretch in improving load bearing capacity and restriction of extension while in use. Glass fabric reinforcement has also been used to maintain dimensional stability and to prevent stretch in higher thickness blankets during printing operations. Elastomers for use as coatings for the printable surface may be nitrile/CR to provide resistance to ink solvents and easy cleaning of blankets which have a high surface finish.

Polymers such as polysulfide rubber and PU may be used to make the printing surface. The essential properties of the rubber compound applied on compressible printing blankets are high hardness, high tensile strength, good resilience, low elongation,

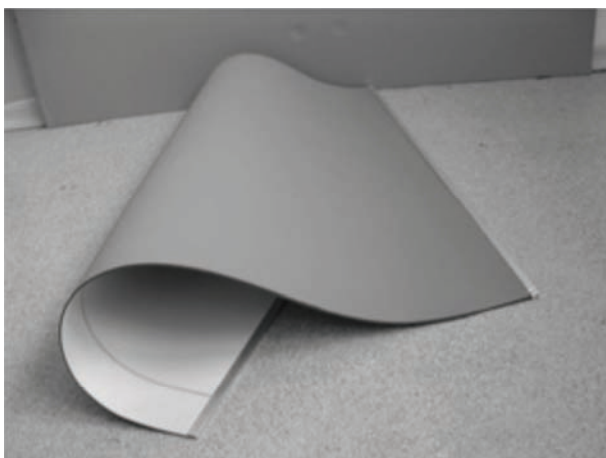
and low compression set to get long-service cylindrical blankets. They should also have the characteristic of quick release of the printable object from the surface [10].

The tubular, gapless and seamless, compressible outer layer blanket with circumferentially inextensible material reduces the vibrations and slippage of a printing press to control smearing of a printed image on a printed product. A removable cylindrical printing blanket is mounted on the blanket cylinder fully assembled. Compressed air is applied to expand the sleeve for installation and removal of the blanket from the cylinder.

Two fabric inner layers with a specific rubber coating are used. The thickness of fabric used is 0.2-0.35 mm. The total thickness of the blankets ranges from 1.65 mm to 3 mm. The thickness of the outer rubber layer is maintained in the range 0.25-0.8 mm.

In between the first fabric layer and the second layer, an adhesive layer is applied to improve the adhesion properties of the coated material.

To produce good printable products, accuracy in the surface thickness and accurate gauge control of the blanket are of primary importance, with mean roughness of the surface being maintained  $>0.6 \mu\text{m}$  but  $<0.95 \mu\text{m}$ . The outer printing layer transfers the image of printing from a mounted plate cylinder to the printed product paper/textile [6]. A representative sample of a rubber offset printing blanket is shown in **Figure 6.9**.



**Figure 6.9** Rubber printing blanket

### **6.3.5 Pollution Control Equipments**

Glass fibre woven fabrics coated on both sides with EPDM/silicone rubber compound can be used to withstand high temperature. They are unaffected by exhaust gases, chemicals and have high abrasion resistance. These coatings on glass fabric are suitable for making ducting for pollution-control equipment used by various industries.

Before coating with rubber, glass fibres are treated with an appropriate bonding agent (proprietary bonding agents are commercially available) to get the desired bond strength between rubber and substrate. Rubber coatings can be applied by calendaring on the treated fibre surface following the dry coating system. Curing can be conducted in long steam heated hydraulic presses in section lengths.

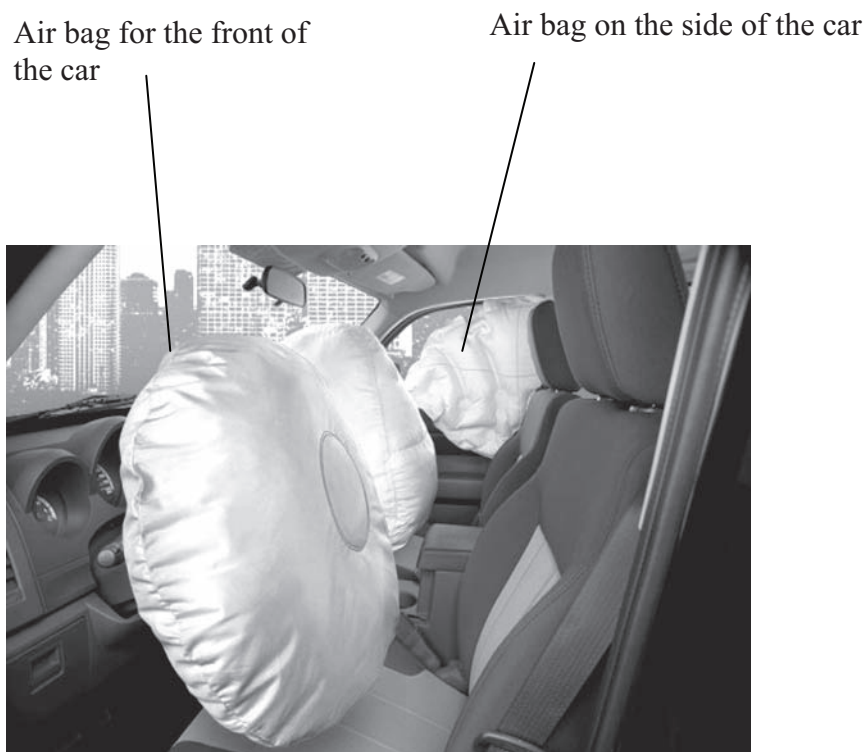
On fabrication of the ducts as per required design and dimensions, the vulcanised coated fabric can be cut from long length-coated material and the edge joints can be made using self-cured rubber-based adhesives.

### **6.3.6 Automobile Crash Cushion: Airbags**

Rubber coated textiles are used as safety devices in automobiles for driver and passengers. The airbag is an inflatable rubber envelope designed to protect automobile occupants from serious injury in the case of collision. The device is fitted inside a vehicle on the steering wheel, dashboards and even on door panels. The airbag blows into a soft pillow during a car crash, minimising the impact to the driver/passenger to prevent injury.

The system consists of an airbag fabricated from rubberised Nylon fabric in a circular manner or in tubular designs provided with an inflator or gas generator, crash sensors, a diagnostic monitoring unit, a steering wheel connecting coil, and an indicator lamp. These components are interconnected by a wiring harness and powered by the vehicle's battery. Driver side airbag and passenger side airbags are legally required to be fitted for all cars and light trucks.

The raw fabric used is scoured and heat set; an elastomeric coating is administered with suitably compounded CR or silicone rubber compounds. Nylon 6 or Nylon 6,6 and polyester fabric is considered suitably tough and flexible for use as the major material in this application.



**Figure 6.10** Passenger car air bags in inflated condition

A silicone rubber-based protective coating is desirable to get lighter, thinner and softer material, and it is more compatible with Nylon fabric. Silicone rubber compounds provide a protective layer against hydrolysis and are chemically inert. Aramid fibres (Kevlar) coated with PTFE (Teflon, DuPont) may be used as a more durable material to make these kinds of bags.

The bags may be made in different shapes and sizes depending on the specific requirement of the particular vehicle. Side-impact airbags are usually mounted in the car door panels and deployed towards the window during impact to protect the head of the passenger.

The chemical propellant consists of sodium azide mixed together with an oxidiser (a substance that helps the sodium azide to react when required). When a sensor detects a severe frontal crash, the sodium azide rapidly inflates the bag by a reaction

and conversion to harmless nitrogen gas, preventing serious injury to drivers and passengers. The crash sensors are designed to prevent the air bag from inflating when the car goes over a bump or a pothole, or in case of a minor collision [11].

Different designs of automobile's crash bags in the inflated condition are shown in Figure 6.10.

## **6.4 Coated Fabrics in Engineering and Architectural Uses**

### **6.4.1 Inflatable Products**

#### **6.4.1.1 Rubber Dams**

Rubber inflatable dams are being used in many countries to temporarily control the level of water in rivers. These coated textile inflatable dams are made of very high tenacity Nylon fabric coated with high water resistance CR compounds. The elastomer mix is coated on both sides of the Nylon fabric and pretreated with a suitable bonding agent. A primary/anchor coating can be applied in the solution spreading method, and subsequent rubber coating on both sides of the textile can be undertaken in a calender machine.

The coated textile is vulcanised in roll form. It can be cured in long hydraulic presses or in the Rotocure system.

Cured fabric should be flexible and have very good wear and high weather-resistance properties. It is then cut according to the suitable templates in constructing the cylindrical structure of the dams with the help of rubber adhesives for the joints. The joints are properly ground for better adherence, and the edges sealed and made leak-proof. The joints may be adhered with self-cured rubber adhesives or a heat-cured rubber solution. In the latter case the joints are cured in long, electrically heated clamp presses. The dams can be made in sections of 1–3 m in height, and the length may be 40–100 m. Cylinders are inflated with compressed air or water ideally at ~27–69 kPa pressure. To carry out rapid inflation and deflation of the cylinders, air filling is preferable. The dam can be installed across channels, in streams and river beds anchored with concrete slabs onto the river bed or bolted on a concrete cased floor. These dams are used to control floods and for the diversion of water for irrigation. They can prevent intrusion of salt water into fresh water by inflating and deflating of the rubber cylinders.



Built-up rubber dams may be damaged due to hydrodynamic instabilities as well as recurrent abrasion caused by the impact of debris carried by the huge flows of water (particularly in the deflated condition), which may result in puncture of the barrier. The coating membrane and the reinforcing member should be of very high abrasion-resistant compound and textiles, respectively. Very high mechanical properties of the coated material are desirable to make a rubber dam which can withstand severe impact.

The durability of the dam should be excellent and should remain serviceable for many years. These dams have been installed in many countries, and remain in working condition [12]. The inflatable rubber dam and its cross-section in the inflated condition are illustrated in **Figure 6.11**.



**Figure 6.11** A rubber dam and a cross-section of the dam in the inflated position

#### **6.4.1.2 Floating Bridges**

The floating temporary bridge is an excellent example of the engineering application of rubber-coated fabrics. Boat-shaped inflated assemblies of separate float units are fabricated from CR coated single/double-ply Nylon 6,6. The individual boat-shaped floats are fitted with various metallic components, Nylon ropes and other fittings, and finally assembled to form a floating bridge. High breaking strength Nylon 6,6

fabrics are utilised in coating and construction of the floating bridges and must have the following properties:

- Breaking strength of Nylon fabric ( $5 \times 20$  cm strip) should be 400 kg (minimum).
- Tear strength should be 20 kg (minimum).
- Peel strength should be 10 kg.
- Weight of coated fabric should be  $700 \text{ g/m}^2$  (maximum).

A coating based on CR compounds is usually achieved using the solution coating method on a rubber spreading machine. The purpose of using this wet process is to get a high air pressure-proof coating and to get high bond strength between the rubber coating and fabric substrate [6].

This type of coating process also helps to prevent porosity. If porosity is present in the initial coating, it can be covered up during subsequent coating applications. Prevention of porosity or leaking out of pressurised air in inflated conditions is imperative if the inflated bridge is being used under high air pressure for long periods of time. Nylon fabric must be treated before coating or chemical bonding agents can be added to the base coating of the textile to obtain the desired fabric-to-rubber adhesion.

Several layers of coatings are applied one after another until a specific thickness is attained. In between coatings, appropriate drying is necessary to evaporate the solvent. This is achieved by passing the coated fabric over the steam chest fitted just after the coating knife on the roller system. The coating finished fabric in the unvulcanised state can be double plied by passing through a set of two rolls fitted in line under mechanical/pneumatic pressure. Green-coated material is dusted with a dusting agent, rolled on high-diameter metal drums and vulcanised in an autoclave. The coated fabric can also be cured in a long hydraulic press heated with steam circulation.

Individual floats are constructed by cutting out from the cured fabric suitably marked with templates before cutting according to the specific design. Seam joints are roughened usually with a hand grinder, and self-cured rubber solution is used for joining. The joints are made leak-proof by applying leak-proof rubber-based putty along the seam line.

The boat-shaped compartments are inflated with air, and assembled together to produce a long floating bridge. The whole structure remains floating on the river/canal for use by the military during assault operations. During assembly of the inflated structure, the flooring of the bridge is made of aluminium panels fitted in such a way, that a battle tank or heavy military vehicles can pass over the bridges without difficulty. This type of bridges is also known as a 'pontoon' bridge where

flat-bottom portable boats/floats are used in building temporary floating bridges [1]. An assembled floating bridge is shown in **Figure 6.12**.



**Figure 6.12** Floating assault bridge

#### **6.4.1.3 Inflatable Domes**

A portable air-inflated observatory made of high tear resistance thin Nylon/polyester fabric coated on both sides with flame-resistant CR-based compounds has been constructed. It provides a fascinating example of the use of rubber-coated fabrics.

The inflated planetarium dome is portable and can be installed in remote areas and villages to demonstrate scientific and educational topics to schoolchildren. A portable digital projector can display objects on the hemispherical top surface of the inflated dome and spectators can observe the programme while sitting inside. Planetarium domes are very popular for astronomical education for demonstrating the grandeur of the night sky. Hence, the colour of the coating should be grey so that it can enhance the black colour of digital projectors to the actual black night sky.

The dome is made without a floor, which allows easy emergency exit. People can enter from a tubular tunnel made from the same coated fabric as the dome.

A high velocity, adjustable electric fan can inflate and erect the dome within 5-10

minutes. The fan can operate after inflation at a slower speed to serve continuous fresh air and to keep the dome inflated. Air passage from the fan is provided by a tubular tunnel made out of the same coated fabric. The usual dimensions of a dome are a diameter of 4–7 m, and the height ranges from 2.5 m to 4 m.

Close woven Nylon fabric is used to fabricate the dome. Both surfaces are coated with fire-retardant rubber. A thin rubber coating is applied on chemically treated Nylon for improved adhesion, so construction can be conducted by a rubber spreading method. After vulcanisation, the coated material is cut according to the design of the dome. Seam joints are made using a self-curing rubber solution. Other accessories for erection of the equipment are supplied with the finished dome [5].

The entire dome can be deflated easily, folded and carried in a bag made out of same fabric material also supplied with the finished dome for transportation. An example of an inflatable dome is shown in **Figure 6.13**.



**Figure 6.13** Planetarium dome in inflated condition. Reproduced with permission from Digitalis Education Solutions, USA

#### **6.4.1.4 Pneumatic Fenders**

Textile rubber-coated pneumatic fenders are used as anti-collision devices in maritime applications. Compressed air filled cylindrical shaped fenders are used as a protective medium against collision if ship-to-ship contact may occur or during berthing operations, both for commercial purposes and by the military. The function of dock fenders is as cushioning material when a ship is being moored. They act as massive energy absorption devices with low unit surface pressure acting upon the ship. Pneumatic fenders are widely used as a protective medium in large tankers, ocean platforms, large docks, harbours and wharfs if a ship comes alongside a quarry or the ship comes to the side of another ship on the sea.

A rubber pneumatic fender is usually a barrel shaped body consisting of high water- and weather-resistant skin members, a rubber-coated Nylon cord in layers (coated with seawater-resistant CR-based compound) embedded in the skin member, and a bead ring is embedded in the rubber-coated cord layer for mounting electronic devices on. Inclusion of sensors in the fender allows information to be read in real-time.

A transponder includes information for identifying the fender (e.g., date of manufacture, installation date, name of customer, place of installation, dimensions, initial air pressure, records of repair and inspection). This system can receive the particulars intrinsic in each fender from the computer, and can manage a fender installed in a wide specific area or in a remote area on the basis of its information.

Pneumatic rubber fenders are manufactured from CR coated textiles as the outer casing and an all rubber air bladder made from NR/butyl rubber built separately and inserted as an inner inflation device to hold air under pressure. Nylon cord used in making tyres can be employed to make cord-reinforced pneumatic fenders. The cords are usually coated with NR - a rubber layer of  $\geq 5$  mm is necessary to insulate and protect the cords. To obtain appropriate adhesion strength with the rubber insulating coating of the Nylon cord, it is necessary for pretreatment of the cords by first dipping in resorcinol formaldehyde latex mix. A 2/3 ply of such coated cord is embedded between the CR-coated textile on the top and bottom parts, which are integrated as a skin membrane.

A CR coating and a Nylon cord composite are preferred because they are unaffected by seawater. The rubber compound as formulated should have excellent resistance to seawater, atmospheric ozone, and ultraviolet (UV) light.

In making an outer casing of a pneumatic fender from cured coated fabric, a self-vulcanising rubber adhesive is used to make the cylindrical shape of the outer casing. The two ends of the made-up barrel are closed by fixing two circular rubber-coated

discs cut from the same coated fabric with the help of a CR-based adhesive. An opening on the lateral side is provided to insert the all rubber bladder for air inflation. High breaking strength Nylon cord lace is passed through the metal eyelets riveted at the lateral opening to help close the opening after insertion of the inner bladder. A non-return metal valve similar to that used in inflation of motor car tyre valves is fitted at the one end of the inner bladder, which protrudes out from the outer casing for use in inflation and deflation of the fender.

Pneumatic fenders are fitted with a swivel shackle at each end connected by an integral tension cable for fitting when in use. Suitable rubber-coated fabric patches with the help of adhesives are placed to seal the outer area of the metallic circular-shaped base of the swivel shackle and valve at both ends of the outer casing to fix the valve in place. Appropriate preparation of the metal and rubber metal bonding agent is necessary while fixing the metal parts on the body of a rubber fender. The outer colour of fenders is usually black, light-grey, or creamy white [13].

If used in heavy offshore berthing locations, the outside of the fender is covered with used rubber automobile tyres and fitted with metallic mesh to provide additional protection (Yokohama type). The tyre net-type fender is highly durable in rugged berthing operations, and the operational life expectancy of a pneumatic fender is ~10-15 years.

In the USA, fenders are designed and fabricated for a particular class of ship so as to absorb more energy when in use. Fenders are fixed with bolts to a structure. Floating fenders are used when floating on the sea and tied with a chain to a quay or ship.

To make the fender universally acceptable, fenders are manufactured in accordance with the specification prescribed in the ISO 17357: 2002 standard.

The following are the desirable properties of a cylindrical pneumatic rubber fender:

- Very high tensile strength and excellent physical properties.
- Pre-tested for loadbearing and energy absorption capacity.
- Resistance to wide range of temperature, ozone and ultraviolet light.
- Excellent anti-ageing property.
- Resistance to seawater corrosion and water swelling.
- Resistance to growth of weeds and creatures found in the sea.
- Virtually no maintenance is required, only occasional topping up of air pressure.

While in use, the fender should have the following characteristics:

- Suitable for use in a wide range of applications.
- Easy to install, service, store (in deflated condition) and replace.
- Good adaptability of transverse and longitudinal movements of ships during mooring.
- Low reaction force, less surface pressure, and reasonable energy absorbability.
- May flow under pressure with the ability to recover the original shape.

Rubber pneumatic fenders are manufactured as per the sizes required by users for specific application areas. The usual size ranges from a diameter of 300 mm  $\times$  600 mm length with a total weight of 8 kg to 3300 mm diameter  $\times$  6500 mm length and a total weight of 2100 kg. These fenders are initially inflated at an operating air pressure of 80-140 kPa.

Rubber pneumatic fenders have unique characteristics of energy absorption. They are highly efficient because the whole strength is provided on the surface. They also exhibit excellent recovery of shape.

General specifications for the manufacture of standard pneumatic fenders include:

- Material for fabric coatings (outer casing) - CR rubber compound with high seawater-resistant property.
- Breaking strength of woven Nylon textile: 200 kgf (5  $\times$  20 cm grip) minimum.
- Weight of coated material: 600 g/m<sup>2</sup>.
- Adhesion strength: 5 kg/25 mm width specimen.

Nylon cords used for reinforcement of fenders are within 840-1300 denier so as to provide adequate strength and flexibility when coated and used in the construction of fenders [12]. A Yokohama design rubber fender is shown in **Figure 6.14**.

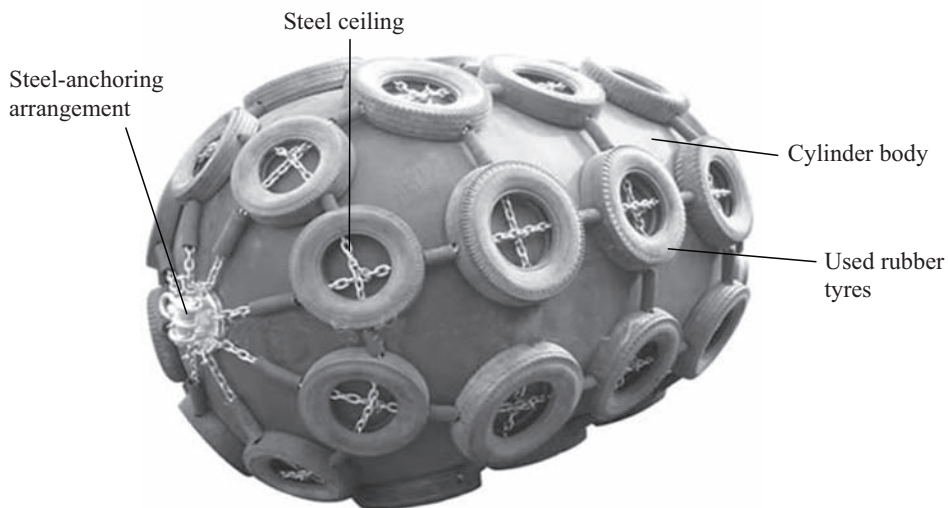
#### **6.4.1.5 Testing of Air Permeability**

The transmission of air/gas through a rubber membrane when coated on both sides of textiles is low. A small dissipation may, however, produce an adverse effect in many applications (e.g., inflatable dams, inflatable dock fenders, inflatable floating bridges, fuel tanks). Permeation through the rubber matrix is by absorption and diffusion.

Permeation of air/gas takes place through the elastomeric membrane in two stages: (i) gas dissolving in the elastomer coating (ii) dissolved gas diffusing through the membrane.

Gas permeability is measured by setting up a pressure differential across the test piece and measuring the amount of gas passing to the low pressure side of the system. BS 903, Part 29 refers to a test procedure of permeability and porosity to gases.

In a water vapour permeability test, a piece of coated fabric is tied around the rim of a small vessel containing desiccant. The assembly is placed in air at an atmosphere of known relative humidity for a period of time. The permeability is measured from the increase in weight of the assembly because of the water vapour passing through the coated material and being absorbed by the desiccant. Thus, the breathability parameter of the coated fabric can be determined.



**Figure 6.14** Yokohama rubber fenders with a meshwork of used tyres and steel rope ceiling



#### **6.4.1.6 Rubber-coated Fabrics in Biotechnology Applications**

The biotechnological application of rubber-coated fabrics is in making portable collapsible biogas plants utilising cow dung or animal manure to generate fuel gas. It is a unique application of elastomeric-coated textiles to be used in remote areas and villages to save fossil fuel and control the ecological balance. A cylindrical tank is constructed (size depending on the requirement) using rubberised fabric usually of cotton fabric coated on both sides with NR.

Cow dung mixed with water is poured into the tank through a funnel made of rubberised fabric fitted on one side of the upper periphery of the tank, and allowed to decompose for a certain period of time. On decomposition of the dung, methane gas is generated.

About 25% of the tank capacity is filled with cow dung-water mixture, thus leaving space for the gas generated during decomposition of the dung. The methane gas is then taken out through a narrow metallic outlet nozzle fitted on top of the tank with the help of a rubber tube (internal diameter, 10 mm). The neck for feeding can be tied with a string when not in use to prevent gas coming out from the opening. The gas can be conveyed to a gas stove for use in cooking or can also be used for lighting purposes; a control valve is fitted on the metal nozzle to control the flow of the gas. From cow dung and other animal manure, depending on the size of the tank, 3-255 m<sup>3</sup> of methane can be generated. It can be used for cooking and heating purposes in the most economical way in remote areas where electricity and fossil fuel are not available.

Certain kinds of bacteria are responsible for the decomposition of cow dung slurry. Two kinds of organic decomposition can take place (i) aerobic (in the presence of oxygen) and (ii) anaerobic (in the absence of oxygen). From 1 kg of cow manure, ~0.06 m<sup>3</sup> of gas may be generated, and the heat value per m<sup>3</sup> of this gas is ~635 kJ.

The gas produced from cow dung contains 55-65% of methane, 30-35% of carbon dioxide and ~2% of nitrogen. The quality of gas may be improved by filtering it through limewater to remove carbon dioxide and calcium chloride to extract water vapour.

About 6 m<sup>3</sup> of gas is equal to 4.5 litres of gasoline. The manure produced by one cow in one year if converted to methane will give the equivalent of 227 litres of gasoline. After the gas is generated, the sludge produced can be used as organic fertiliser because it contains nitrogen [14].

The equipment can also be used for decomposing vegetable and plant waste. The equipment can be washed, deflated and transported easily as a lightweight portable

tank to another location. By the decomposition of organic material, millions of cubic feet of biogas or methane can be generated to help save the use of fossil fuels.

NR on higher breaking strength cotton textiles (usually twill weave fabric) may be used for coating and fabrication of the tank. The rubber compound for coating should be of high weather resistance because fabricated tanks are used outdoors. The seams of the tank must be appropriately adhered during fabrication using solvent-based rubber adhesives to ensure gas does not leak under moderate pressure.

The discarded tank can be buried in the soil because it is made of biodegradable material such as NR and natural fibres. For increased durability in outdoor installations, the coating can be made from CR compound on lightweight Nylon fabric [15].

### **6.4.2 Non-inflatable Items**

#### **6.4.2.1 Roofing, Pond Lining and Rainwater Harvesting Coated Fabric Membranes**

Barriers against water migration elastomeric sheeting made from butyl rubber and CR have been used for some time. EPDM polymer-based all rubber membranes are an alternative system widely used as protective layers for roofing applications.

EPDM-coated fabric on a natural or synthetic substrate can give excellent, highly durable performance when used as a roofing membrane, and in other waterproofing applications in construction industries.

Superior weather- and oxidation-resistance properties, excellent impermeability to water, high resistance to chemicals, and overall economy of use make these EPDM-coated fabrics the material of choice for improved waterproofing and for protective linings.

Coating of this polymer on woven textiles can be conducted by applying rubber dough on fabric in a spreading machine as anchor coating. The subsequent coating can be conducted on a three-roll calendering machine one side at a time or in a four-roll machine to coat both sides in a single operation.

EPDM compounds, alone or blended with NR/SBR (which will enhance the weather, ozone, and chemical resistance of the blends) can be coated on natural or synthetic textiles. For synthetic textiles, treatment with an appropriate bonding agent is necessary to get the desired adhesion.

Commercially available grades of EPDM are composed of 4-5% by weight of diene and 30-70% by weight of ethylene to get serviceable coated materials. With increased ethylene content, the final coated product shows higher hardness, higher tensile strength, and exhibits no degradation in tensile strength up to 125 °C when aged for 1,500 hours.

The ultimate life of a building depends on the reliability and the quality of the roofing system it has been provided with. EPDM-coated textiles can provide highly durable, very long periods of protection of ~30 years as a protective barrier for waterproofing if used on a building roofing system. They can prevent water seepage on rooftops, vertical walls, grounds and basement walls in construction applications [16].

For all-rubber membranes used for these purposes, 1-1.5 mm-thick sheeting may be required. However, in coated textile items, it is sufficient to use 0.4-0.6 mm-thickness materials because the textile substrate provides reinforcement and prevents tearing.

Lightweight cotton or man-made woven textiles can be used in the range 40–80 g/m<sup>2</sup> by weight. Higher weight fabric may be used depending on the severity of applications.

Its resistance to dilute acids, alkalis, vegetable fats, animal fats, and toxic chemicals, combined with good physical properties, means that EPDM-coated fabric can be effectively used as a lining barrier for effluent treatment plants to prevent toxic materials being absorbed by the soil, thereby protecting the environment.

In many countries, importance is given to harvesting rainwater to meet the lack of water during dry seasons. EPDM or its blend-coated fabric may be used as a protective liner in overhead tanks, underground wells, ponds, and other water reservoirs to prevent seepage/absorption of water by soil. This system of water harvesting can be widely practised for domestic, agriculture and industrial purposes. Thus, a coated fabric may help to save energy because less electricity is consumed to pump freshwater from underground or from water resources in water deficient locations.

Another method of water preservation is by providing water catchment linings with textiles coated on both sides with silicone or EPDM elastomers. The coated fabric can be stitched or edges can be jointed with the help of a rubber solution (silicone rubber-based or EPDM-based adhesive) to construct the entire liner in the shape of a ditch/pond dug out on the earth for storing water for irrigation purposes. The coated surface provides an impervious surface to seepage of water into the soil (particularly in the dry season). The fabric liner used may be of lightweight Nylon to give a long life due to the coated materials resistance to weathering if exposed to the atmosphere.

For economic reasons, EPDM mixes are preferred instead of silicone elastomers because the former can accept a high proportion of fillers and process oils.

In 'green buildings', rooftop terrace gardens are becoming popular because they are thought to improve the working and living environment. In such applications, utilisation of EPDM-coated fabric is most appropriate because of its unique characteristics in preventing penetration of plant roots and micro-organisms.

In highly populated areas such as airports, railway stations, and shopping malls, EPDM-coated textiles can be used thanks to their following properties: noise deadening, high abrasion resistance, highly water- and weather-proof, cleanable and durable with a long service life.

## **6.5 Coated Fabric Inflatable Devices for Use in Therapeutic and Lifesaving Equipment**

### **6.5.1 Air Support Sleeping System**

Cotton woven textiles coated on one side with NR or NR/SBR/PBR blends are used in fabricating inflatable air-filled mattresses. The inner air pressure with a controlled degree of firmness allows tailoring to individual concepts of comfort. The surface of these air mattresses is made in a quilted design and fabricated from unvulcanised rubberised fabrics. Fixing of rubber-coated tapes made to a specific design in the shape of the letter 'P' is adhered on the upper and bottom layer of coated fabric, placing the rubber-coated surface as the inside layer for the formation of the quilted design. The mattress is fabricated using rubber solvents for joining the ends in an unvulcanised state. A moulded rubber valve is fitted at one corner of the mattress with the help of rubber adhesive for inflation and deflation.

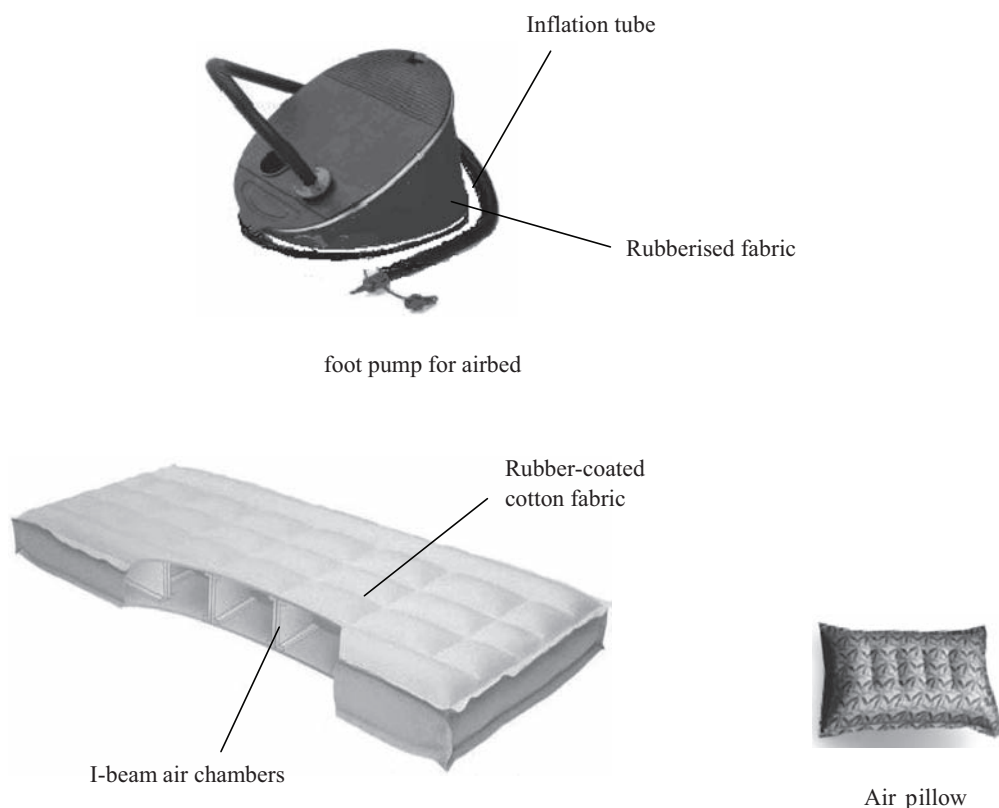
The made-up mattress is inflated slightly and dusted inside with a dusting agent to prevent adherence of the two rubberised inner surfaces during vulcanisation. It is then deflated, spread on a bed of French chalk on a sheet metal tray, and vulcanised in a vulcaniser, an indirect heating system where the steam is circulated through coils inside the vulcaniser and the pressure is created by introducing compressed air. Cured mattresses are fitted with a plastic stopper to the rubber valve, cleaned and packed.

If a person is lying on an airbed with control of air pressure, the contour of the body enables even distribution of the weight of the body, and this provides support to the spine. Air support structures eliminate pressure points, thus improving blood

circulation. Interconnecting air pockets maintain ‘floating’ of the air cushion. Due to these beneficial reasons, doctors and physiotherapists have advised the use of air-inflatable beds [17].

The degree of firmness of the bed can be adjusted by controlling the air pressure with a small electronic air pump to maintain support to the spine. Usually a manually operated foot pump is supplied with the airbed.

Photographs of an airbed, foot pump and ‘I’ beam structure implemented in the formation of air pockets are shown in **Figure 6.15**.



**Figure 6.15** Airbed chambers, foot pump and air pillow

Travellers generally use the most common inflatable items such as air pillows and airbeds. These are made of ST rubberised fabric, usually cotton fabric coated with

NR or blended with general purpose synthetic rubbers. Airbeds, which can be used on beaches for sunbathing, can be made from one-side rubber-coated orange Nylon fabric with inbuilt air pillows of single-bed or double-bed design. An inflated air pillow is also shown in **Figure 6.15**.

Inflatable furniture is fabricated from rubberised fabric using synthetic or cotton fabric coated with NR or blends to provide flexibility. It can be air-inflated with the help of a pneumatic hand or electrical/battery-operated small portable pump. The inflatable can also be filled with many small bean-shaped materials made from expanded polystyrene to provide seating comfort.

Inflated collars or neckbands prepared from ST-coated textiles for long-distance air travellers provide support to the neck to prevent neck pain. The user can rest his/her head on the chair when in the sitting position. Inflated circular air pillows made from rubberised fabric provide back support when sitting on sofas.

### **6.5.2 Water Mattresses for Prevention of Pressure Sores**

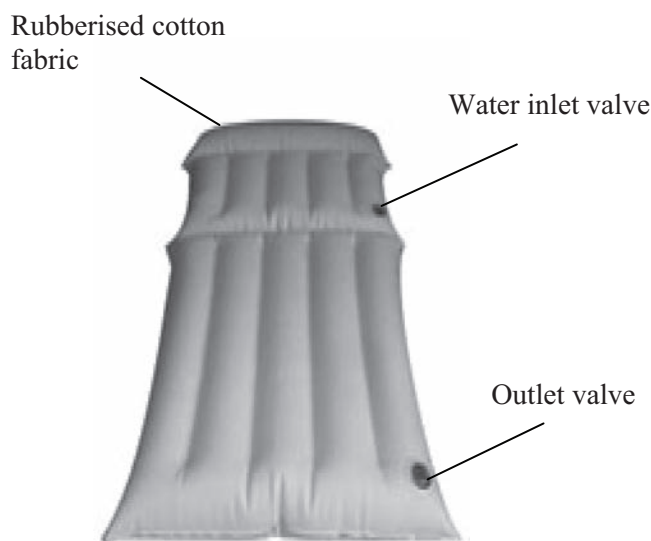
Water mattresses are fabricated from ST rubberised cotton fabric and filled with water. They help to prevent pressure sores. High breaking strength plain weave cotton fabric is usually dyed, proofed with water-resistant NR mixes or blends of NR/SBR and NR/PBR, and coated in a calender with anchor/base coating in a spreading machine to make the proofing fully leakproof. They are then suitable for use in the fabrication of waterbeds or mattresses.

The process of making a waterbed is similar to that for making air mattresses as described in **Section 6.4.1** except for the long channels for water movement and the bed is fitted with inlet and outlet valves.

The mattress should be extremely waterproof in the inner layer and in the cotton woven textile outer layer. Sacks or pocket design spaces inside may be filled with water directly from a tap through the spout provided.

The rippling effect of the bed due to the movement of water inside the sacks of the bed improves blood circulation. This can prevent the development of body aches, back pain and cramps.

By appropriate surface design, stimulation can be provided which is considered to be a useful remedy for skin ulcers or pressure sores if a person is confined to bed for a long time [17]. A cotton fabric-rubberised waterbed fitted with valves is shown in **Figure 6.16**.



**Figure 6.16** Water mattress. Reproduced with permission from Odessey Products, Jammu, India

### **6.5.3 Rubberised Airbags to Monitor Breathing Disorders**

An interesting application of rubber-coated textile technology is the preparation of a medical device. An air filled mattress-like device consists of a series of one-sided rubber-coated cotton fabric tubular structures. They are used to diagnose sleeping disorders due to change in breathing patterns such as apnoea (a transient cessation of respiration and snoring).

High breaking strength, lightweight cotton textiles, usually dyed in a drab colour, are primarily used for coating with a rubber solution in a spreading machine. Sub-coating is usually done in a calender with highly flexible NR-based non-toxic mixes alone or blended with SBR/PBR. This ensures high air-proofing of the coated material.

The tubular structures are fabricated by hand from ST rubber-coated fabric in the unvulcanised state as per the specific design. Tube edges are made slightly overlapped and joined using heat-curable rubber adhesives. Rubber-moulded valves are fitted at the ends for inflation and deflation of the assembled device. All the tubes are vulcanised in a similar way (an air mattress is cured as described in **Section 4.6.1**). All

the individually cured tubes are finally assembled to form a mattress-like equipment.

A patient can be laid on a 2 m long and 90 cm wide bed of airbags, constructed with 12 air chambers inflated by an air compressor. These can have a width of 25 cm, 22 cm and 12 cm, and an inflated thickness of 4 cm. When the patient breathes, there will be slight displacement of weight on the airbags due to the movement of the lungs. This movement of the weight correlates with the breathing pattern of the patient.

The assembled air mattress is fitted with 6-8 PU tubes (inner diameter, 3 mm). These tubes are connected to differential pressure transducers, and the pressure sensors can measure the breathing pattern [17].

#### **6.5.4 Inflatable Splints: Aids for Limb Injuries**

Inflatable splints are 'L'-shaped double-wall casings. They are fabricated from one-side rubberised material on brightly coloured Nylon fabric (usually orange in colour for identification). A rubber spout is assembled with a rubber tube and plastic stopper for use in inflation of the splint. A plastic zip is provided on one edge of the casing for ease of use on the injured limb.

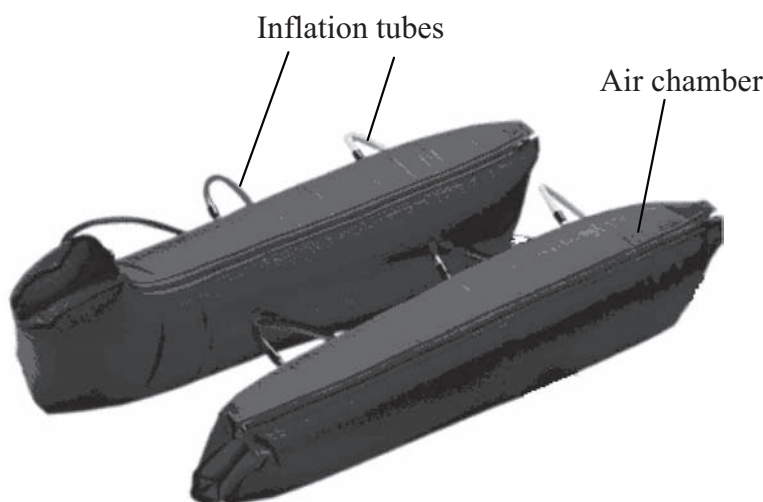
The device is divided into eight segments by fixing rubberised tapes internally between the two rubber-coated inner surfaces. The four partition walls have air chambers, and can be inflated by mouth. Fabrication is conducted using unvulcanised ST rubberised fabric, keeping the uncoated surface as the outer after the ultimate design of the equipment. Curing is done in a similar way to that described in **Section 6.5.1**. A plastic zip is fitted at one edge by stitching after the curing.

The device is mainly used as a temporary measure to secure the damaged limb until the injured person can be taken to a more sophisticated medical facility [17].

By using an electronic intermittently operated air pressure pump fitted to the splint, it can also be operated as massaging equipment. It may help in the early recovery of a patient by mobilising the limb muscles, and can help blood circulation due to postoperative stiffness.

The method of treatment is to put the encasing on the affected stiff part of the limb. The inflation pressure may be maintained at 5-67 kPa, and the cycles repeated at 3-4 cycles per minute. A pair of inflated splints is shown in **Figure 6.17**.





**Figure 6.17** Inflatable splints made from rubberised fabric

#### **6.5.5 Pressure Device for the Treatment of Filariasis**

There is another significant application of rubber-coated fabrics in medical instrumentation: the treatment of chronic filariasis. Filariasis is characterised by gross thickening of the skin and connective tissue caused by blockage of the lymphatic system by infestation with filarial worms. A huge number of people living in tropical and sub-tropical endemic regions have this chronic disease.

An inflatable, highly flexible leg shaped appliance is administered for the management of the disease. The device is a double wall, air-inflatable encasing, fabricated from unvulcanised cotton fabric, coated on one side using a non-toxic NR or NR/SBR blend compound. The device should be made fully leak-proof and subsequently vulcanised. A plastic zip fastener is stitched on the cured casing.

The rubber-coated textile casing is designed to match the contour and shape of the human leg, completely enclosing the limb of the patient. A plastic slide fastener is fitted at the lower halves of the bag for easy application, and two rubber spouts are fitted on the casing. One of them is connected to an electronic air pump which can operate intermittently by inflation and deflation to massage the affected limb. The other rubber spout contains a manometer.

The pump can be set between 100 seconds and 180 seconds. The casing will press the limb for the set time. The maximum air pressure necessary for this treatment is  $\leq 20$  kPa.

It has been proved that pressurisation of lymph at the stage of lymph oedema in filarial infection using this rubberised fabric device can reduce excessive swelling of the limbs.

This device is safe to use for patients suffering from heart trouble, liver disease or kidney disorders if the drugs administered to control filariasis are not safe [17].

## **6.6 Coated Fabrics in the Military**

### **6.6.1 Collapsible Fuel Storage Tanks**

Collapsible rubberised fabric storage containers constructed from elastomer-coated textiles in vulcanised form meet the operational requirements and provide vital logistic support in transporting fuel, water, and chemicals. Fuel containers are widely used by the military for tactical bulk storage of petroleum in military operations. These fuel containers are fabricated from synthetic fabric coated on both sides with highly oil-resistant nitrile rubbers. High breaking strength and high tear strength Nylon fabrics are usually used as reinforcement.

Some of the pillow shaped, custom designed, static collapsible tanks are put into service for storage and transportation of water and chemicals made from TPU, PVC and polyethylene (PE)/polypropylene-coated fabrics.

These ready-to-use versatile containers can be deployed with the minimum of ground preparation. Alternatively, a rubberised fabric may be spread on the site to station the containers to avoid sharp objects which may affect the outer coating.

Collapsible tanks used for carrying and transporting water can also be prepared from rubber- and thermoplastic-coated materials. The inner polymer coating material of the containers should be non-toxic, hygienic, and should resist attack from micro-organisms to avoid contamination of drinking water. There is particular need for collapsible potable water storage containers which are resistant to nuclear, biological and chemical (NBC) warfare.

The range of elastomers used for coating textiles in the construction of these containers depends upon the end use. For example, NR or blends of NR/SBR/PBR compounds

would be used for making water storage tanks. For chemical storage, the preferred choices would be from the elastomers butyl rubber, EPDM and CSM.



**Figure 6.18** Collapsible fuel tank made of rubberised fabric with a capacity of 300,000 litres

For fuel tanks (which are the most critical), high acrylonitrile-butadiene rubber compound-based coatings on both surfaces of the textiles can offer significant service properties. As an outer coating to improve weatherability, CR-based coatings give good results.

The fabric-to-rubber adhesion and seam adhesion strength need to be assured before utilisation of the cured materials in fabrication of the tank. During construction of the tanks, the technique of joining the seams by preparing with proper grinding of the edges as well as adequate overlapping is necessary to meet the specified seam strength of the coated material.

Proper joining of the seams, leak proofing, and desired seam strength can be achieved by using solvent-based rubber cement and by adding a small amount of liquid bonding agent to the cement just before application. Rubber cement can improve bond strength and offer leak-proof seams.

Polysulfide polymer-based putties/sealants can be applied along the seam lines to make them leakproof. Wicking of fuel oil through the open ends of textile yarns can be prevented by properly coating the woven fabric, and by ensuring penetration of the elastomer coating into the interstices of the fabric. To prevent wicking, the solution coating may be increased to achieve the required thickness of coated fabric.

After the coating is complete, the coated material is visually inspected for any uncoated surface or damage sustained during coating. Those areas can be repaired and dusted with talcum powder to prevent sticking, then wrapped on higher diameter metal drums and vulcanised in a steam heated vulcaniser. Alternatively, the coated textile can be cured in long steam heated hydraulic presses or in a Rotocure machine.

For collapsible water containers the seams may be heat-sealed when coated with thermoplastic materials. PU-coated fabric is radio frequency (RF) sealable as long as there are fill and discharge valves as well as a vent. The capacity range of these water tanks can be made to be 1 m<sup>3</sup> to 100 m<sup>3</sup>.

Oil-resistant rubberised fabric static fuel storage tanks are designed and engineered to meet specific dimensions and capacity. They are available in the capacity range of 25 m<sup>3</sup> to 250 m<sup>3</sup>.

To meet a user's specific needs, the filling and discharge valve assembly for draining and filling are supplied as a package to meet the operational requirements of the tank.

Other ancillary equipment such as pumps for filling, oil-resistant hoses, Nylon webbings to harness the tank to restrain surging of the container due to movement of the liquid, and ratchet accessories are also supplied with the tank.

The maximum wetted service life of a collapsible rubberised fabric tank if petroleum is introduced into the tank is three years under ideal conditions, and the shelf-life is five years as stated by the manufacturers. The useful life of a petroleum storage collapsible rubber tank is subject to inspection and testing at regular intervals to investigate technologies to extend the service life and shelf-life of the equipment.

Weeping of fuel may be the result of the affected coated surface while in use. This may be due to damage to the coating, particularly if a loaded tank is dragged on rough surfaces. This problem must be avoided to acquire a long service life of a container (which is considered to be costly equipment).

The woven Nylon textile suitable for coating with nitrile rubber used for the construction of a fuel tank is Nylon 6 or Nylon 6,6 with the following specification as guidelines:

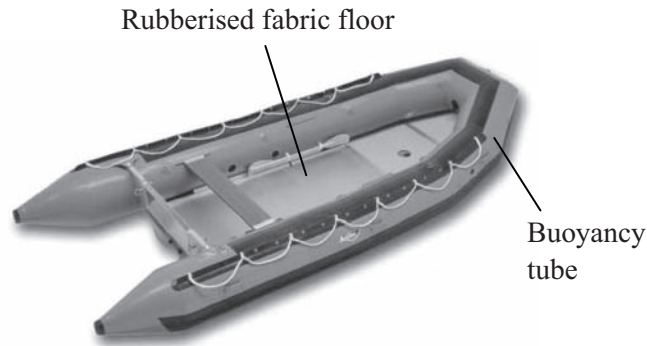
- Breaking strength should be 450 kgf (5 × 20 cm strip) minimum.
- Seams shear strength should be 350 kgf minimum.
- Tear strength should be 45 kgf minimum.

There is a continued quest by the military for improved materials and lighter, more durable fabric, so innovative manufacturing processes are needed [13]. A photograph of a collapsible fuel tank in the inflated condition is illustrated in **Figure 6.18**.

### **6.6.2 Inflatable Boats and Aeronautical Life Raft Survival Equipment**

Polymer-coated fabrics are the major material in the fabrication of inflatable boats. Rubber inflatable boats are constructed from water resistant PE/CSM rubber coated on synthetic fabrics. The fabric coating is done with properly formulated high water- and weather-resistant rubber compounds on woven Nylon/polyester fabric using a solution coating process. In a rubber spreading machine, the number of coats may be increased to get the desired thickness of coating. The spreading process is desirable because it makes the textile fully leak-proof. There should not be any leakage at high air pressure. A base or anchor coat may be applied on bonding agent treated synthetic fabric to improve adhesion strength to the subsequent coating in the calender. A black CR coating is usually used for boats. However, for brightly coloured boats such as recreational and sports boats, CSM rubber compounds are utilised thanks to their excellent colour retention. A bright colour coating as the border on the outer periphery of black boats is sometimes applied using CSM rubber-based paints for identification from a distance if the boat is at sea. The outer rubber coating should have high abrasion and UV ray resistance, and the inner layer must have high air retention.

The prime reinforcing member is the fabric used in making the boats, the strength of which is measured by the weight of the thread used in construction of the textile. Denier or decitex (DTex) is the unit of measurement (1 denier of a yarn is the weight in grammes of 9000 m, and the DTex is the weight in grammes of 1000 m). Heavy-duty boats for higher carrying capacity may be constructed from 1000-1600 denier fabric, with the lighter variety using 200 denier fabrics. The tightness of the weave is another measure (threads per cm<sup>2</sup>), and the weight of thread is important when considering weave density [18].



**Figure 6.19** Inflatable rubber boat (five person capacity)

In the making of lighter weight boats, PU- or PVC-coated fabric can also be applied. The method of joining PU-coated fabric is by a thermobonding system.

Manufacturing a rubber boat from a coated textile and assembling its different shapes of cut components is a skilled hand operation. The edges of the cut panels of the desired pattern are roughened by machine/hand grinding, cleaned with solvent, and the two edges are adhered together with the help of self-cured adhesive with an overlap to obtain high seam joint strength in buoyancy tubes.

A rubberised fabric tape is applied along the seams to ensure leakproof joints. The floor of the boats is made of tough rubberised fabric. To get rigidity, plywood or aluminium panels are inserted between the two side tubular structures. A wooden rigid cross board or transom is provided for mounting the outboard motor. The buoyancy tubes are constructed in a tubular shape in separate sections, and fitted with metallic/plastic valves for inflation/deflation of air. Some of the inflatable boats are fitted with inflatable 'V'-shaped keels. This will help the hull to move through waves, reducing the slamming effect caused by the flat hull when the boat is moving at speed over the wave.

Inflatable rubber boats are used for whitewater rafting, kayaking, lake touring and ocean touring. Heavy-duty rubber inflatable boats are operational as assault boats used by the military, coast guards, and other defence forces as rescue boats.

Usually the rubber inflatable boats are 2-7 m in length, with a carrying capacity ranging from 6 to 20 persons, and they are propelled by outboard motors of 4-60

kW. In whitewater rafting, and on riding it at a slower speed, hand paddles made of wood or fibreglass are used.

Different designs of rubberised fabric, brightly coloured inflatable boats are in use such as:

- Rescue craft
- Dive boats for scuba diving
- Recreational, commercial and fishing boats
- Military craft

The common term used for rubber inflatable boats is ‘rubber dinghy’ and ‘Zodiac boat’. Development of rigid-hulled inflatable boats (RIB) with a rigid floor and solid hull can cut through waves more easily, offering a comfortable ride. An inflatable rubber boat is shown in **Figure 6.19**.

In the USA, the term ‘Zodiac’ is named after the pioneer in the manufacture of inflatable boats. Zodiac boats are widely used for RIB inflatable boats manufactured under safety of life at sea norms [19].

### **6.6.3 Life Rafts**

Marine life rafts are manufactured from rubber-coated textile fabrics and are used to save lives at sea if the crew of a ship is disabled. They are built to be tough and durable with double buoyancy tubes, a self-erecting canopy and an insulated double rubberised fabric floor. Life rafts are designed with a self-inflating device. This can be fully inflated within 15 seconds if it comes into contact with seawater with the aid of CO<sub>2</sub> gas cylinders and a sea activated battery. The battery activates and punctures the CO<sub>2</sub> cylinder within seconds, inflating all of the raft buoyancy chambers. Buoyancy tubes are constructed from high tenacity Nylon fabric coated on both sides with water-resistant CR-based compound following military specifications. Butyl rubber-coated fabric can also be used to construct buoyancy tubes. A raft can be made to accommodate 6-25 people.

Two door openings are provided in a raft to offer air circulation. Rafts have two buoyancy chambers so that one can remain operative if the other one is damaged. The canopy provides protection from the weather, and the floor, being attached firmly with buoyancy tubes, provides accommodation to the survivors. The tube is divided into two bulkhead compartments for redundancy if punctured, and is supplied with a CO<sub>2</sub> inflation system, outside lifelines, and survival kit. Reflective tapes (3M, Scottie)

are available in sewable-type or one side-coated with pressure-sensitive adhesive fixed on the visible surfaces of the rafts. These tapes help to enhance visibility to this life-saving equipment at night or low light conditions when searching and can be illuminated by spotlight or other light sources for identification by the rescue team.

Highly durable, high breaking strength Nylon fabric meeting the military standard specification is coated with CR or butyl rubber compound in solution form on both surfaces of the fabric. The coating can be applied in a rubber-spreading machine. An increased number of runs in the solution coating may be required to get the desired thickness of the coating and to avoid pinholes on the rubber coatings. The coated fabric is brightly coloured (usually orange, and sometimes with a fluorescent orange outside) for identification purposes, and a coating of a soothing blue colour on the inside to prevent glare [20].

The basic textile fabric used in the construction of inflatable life rafts may be of Nylon, polyester or any other synthetic fabric coated with a suitable polymer which conforms to the following desirable properties:

- The maximum total weight of the coated fabric should be 650 g/m<sup>2</sup>.
- The minimum breaking strength of the coated fabric should be 240 kg (5 cm × 20 cm grip).
- The minimum tear strength should be 90 kg.
- The minimum adhesion strength should be 5 kg (between rubber coatings and fabric).

The coated fabric must be resistant to ocean water and have passed the saline water test before use in constructing the structure. The results of the saline water test of different elastomers is illustrated in **Table 6.1**.

Life rafts can also be made from PU-coated fabric constructed with a RF heat-sealing system to make them lighter in weight. Rafts are manufactured and packed with all survival equipment as per life at sea safety norms and conforming to International Maritime Organisation Resolutions [21]. The entire raft can be deflated and packed in a fabric valise or it can be vacuum-packed. Manufacturers of the equipment offer a warranty of 12 years and a service interval of 3 years. An inflatable life raft with double buoyancy chambers and hood is shown with rescue emergency medicines and accessories in **Figure 6.20**.





**Figure 6.20** Inflatable life raft with two buoyancy chambers (25 person capacity)

<b>Table 6.1 Seawater absorption of different rubbers (duration of test = 24 months at room temperature)</b>	
<b>Rubber</b>	<b>Percentage absorption</b>
Magnesium dioxide-cured polychloroprene	32
Litharge-cured polychloroprene	5
Chlorobutyl rubber	4
Nitrile rubber	5
Natural rubber	4

Aeronautical inflatable life rafts may be deployed from a hovering helicopter at a height of 12-18 meters, the valise being dropped into the sea. As soon as it comes into contact with water, it operates the inflation mechanism and the life raft begins to inflate. The internal gas pressure generated breaks open the valise lacing and the raft becomes fully inflated, and floats on water.

High tenacity Nylon single or double ply coated with CR/butyl/CSM to get high air retention capacity, as well as very good ageing and abrasion resistance is used to

make large boats for navy rescue, sports, and for marine rafts inflated with carbon dioxide gas employed as survival equipment [22].

#### **6.6.4 Life Jacket – Safety Equipment**

Inflatable life jackets are utilised as safety devices if danger from drowning is likely. High breaking strength Nylon fabric dyed in orange or traffic yellow and coated on one side with good air/gas retention is used for making inflatable life jacket stoles.

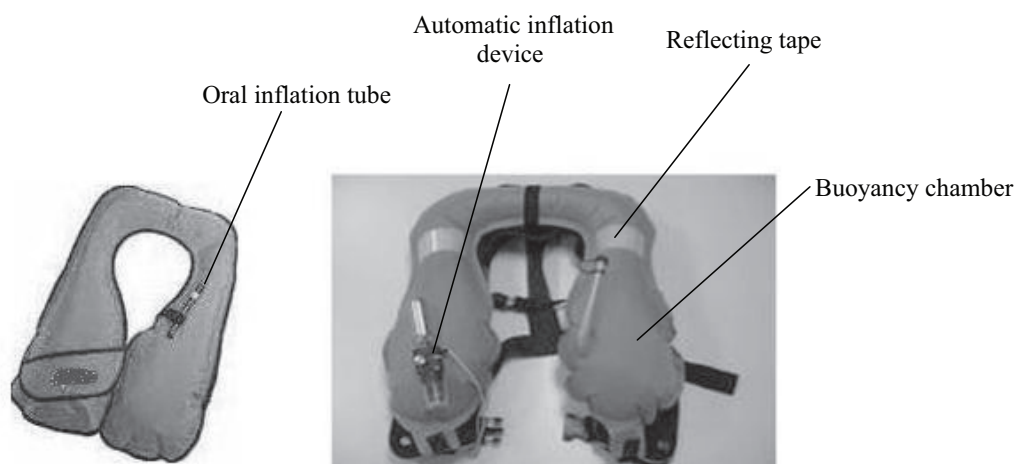
Rubberisation can be of NR or a blend of NR/SBR/PBR mixes in some of the uses. If flame resistance is needed, a CR base compound with flame-retardant additives can be the choice. Liquid bonding agent treatment of the Nylon fabric or incorporation of a dry bonding agent directly into the compound is necessary to achieve the desired adhesion property. Coating is usually carried out in a spreading machine with multiple runs to get the desired thickness, and to ensure high air/gas impermeability [17].

Coated, unvulcanised fabric is cut with the help of made-up templates designed as per size and dimension of the stoles. Fabrication of the stoles or air chambers is usually done by hand with the use of a suitable rubber adhesive. Subsequently, vulcanisation is conducted in an autoclave under steam pressure by hanging individually inside the vulcaniser. After curing, Nylon tapes and webbings as well as other fittings are assembled to make a complete life jacket ready for use. A rubber tube with a plastic valve is provided for oral inflation by the user for manually inflated life jackets and consists of one chamber. The essential property of a completed life jacket is its buoyancy, which should be ~15 kg.

Automatic inflatable life jackets are used by air force crews and paratroopers. They consist of two rubber-coated Nylon stoles, and are inflated within three seconds by carbon dioxide gas from the CO<sub>2</sub> cylinder provided with the jacket assembly (including a water-activated battery to activate the inflation mechanism if a person jumps into the water). The completed life jacket is housed in a collar of Nylon fabric (the same fabric used for the air chambers), which is designed to be worn in the hanging position from the user's neck.

These life jackets are specially designed to provide lateral and occipital support to the head so that the mouth of an exhausted/unconscious person will be clear of water with the body inclined backward from the vertical position at 30° to 60°.

A lifeline made of strong Nylon rope secured with the device is provided to allow an unconscious person to be retrieved by the rescue team.



**Figure 6.21** Oral inflatable life jacket (left) and automatic inflatable life jacket (right)

Life rafts and life jackets are made from brightly coloured fabric inflation side coated with the rubber mix. The purpose of using brightly coloured fabric is for high visibility for identification from a long distance during surveillance by a helicopter or from a ship at sea. Therefore, the colour fastness of the fabric should be as per the specified standard [17]. A manually inflatable life jacket and automatic inflatable life jacket are displayed in **Figure 6.21**.

Life rafts, rubber boats, pneumatic fenders, and life jackets are made of rubber-coated material and are exposed to seawater while in use. Hence, it is necessary to test the seawater absorption properties of basic rubber mixes used for coating.

If immersed in water over long periods of time, all rubbers absorb water. Polychloroprene rubber coated textiles which are usually used in making these products absorb more than 30% of water when normally cured with magnesium oxide. A significant reduction in water absorption can be achieved if this elastomer is cured with a litharge system; the seawater absorption will be as low as 5%. See **Chapter 2** for further details of the litharge system.

### **6.6.5 Anti-Gravity Suit - Life-saving Equipment**

This is a highly sophisticated garment used by combat pilots while flying in high performance aircraft. Rapid changes in the flight direction produces acceleration or positive 'G' (Earth's gravitational) forces which make the pilot heavier, resulting in the draining of blood from the head to lower parts of the body [17].

A reduction in volume of blood in the head of the pilot can result in the loss of peripheral vision and, after a short time, it may cause the pilot to lose consciousness. A total blackout can result in complete loss of control of the aircraft by the pilot, with potentially catastrophic results.

The device is connected with a pressure mechanism in the aircraft that automatically applies air pressure to the abdomen, thighs, and leg areas in proportion to G forces encountered during flying. In this way, it can sustain a proper volume of blood to the head.

The device could raise the threshold level of the pilot by 1-2 G and help in reducing the fatigue caused by the applications of G forces repeatedly when flying in high performance aircraft. An anti-gravity suit and its different parts is shown in **Figure 6.22**.

The anti-gravity suit comprises an intricate design inner bladder system fabricated from all-rubber sheeting or from both side-coated, high breaking strength, thin weight, closely woven Nylon fabric. Coating should be based on a CR-based compound with flame-resistance properties in a spreading machine as a wet coating method. Low viscosity rubber solution with multiple coats is applied to get the desired thickness. The fabric which is coated on both sides is vulcanised, and cut with the help of design templates as per the dimension of the finished suit. It is then fabricated to the shape of the inner bladder using suitable room temperature cured rubber solution. The coated fabric must be tested for leak proofing under air pressure, and should be highly flexible.

The outer casing of the suit is usually cut from olive green coloured, high breaking strength Nylon fabric as per specific dimensions and stitched in a textile sewing machine to give shape. Finally, the made-up bladder is inserted and the stitching of outer Nylon casing made complete.



**Figure 6.22** Anti-gravity suit

### **6.6.6 Helicopter Landing Pads**

Helicopter landing pads are prefabricated membranes made from rubberised fabric used for surfacing to facilitate the landing of a helicopter on uneven or rough surfaces. It works as a dust-proof, smooth membrane surface when a helicopter lands on soil. CR-coated Nylon fabric anchored in such a fashion on the ground with a suitable means of fixing allows a helicopter to land in places where there are no proper airstrips available for operational/rescue purposes. The coated material must have very good resistance to weather, fuel spillage, flame, heat and low temperature. The choice of elastomer for coating woven textiles should meet the desired physical properties necessary for fabrication of the product.

The coating on the fabric can be done with suitable mixes of CR-based compound on Nylon fabric in a rubber spreading machine. A base or anchor coating in solution form can be applied by adding with suitable bonding agent to improve the adhesion strength of elastomer matrix with the base fabric. Alternatively, pretreated synthetic fabric can be used for coating. The desired thickness of coating may be achieved

by increasing the number of runs in the spreading machine or in the calender after anchor coating. After completion of the coating, it is liberally dusted with French chalk, or a thin fabric liner can be used to prevent sticking. The curing can be done in roll form in a steam heated autoclave or it can be press cured in long hydraulic presses in the section curing method.

The landing pad is fabricated from the cured, coated material, cut into specific dimensions as per the requirement of the users, and fitted with anchoring arrangements. Folding of the edges and adhesion is done using a rubber-based adhesive. After finishing, the dimensions are measured as specified by the user.

The edges of the finished pads are fitted with eyelets and fasteners to facilitate installations. A fabric-reinforced helicopter landing pad is displayed in **Figure 6.23**.



**Figure 6.23** Helicopter landing pad

### **6.6.7 Nuclear, Biological and Chemical Protective Clothing and Protective Gear**

NBC weapons exploited in warfare are very destructive, the effect of which go beyond the intended military target. Therefore, these weapons are called ‘weapons of mass destruction’.

Nuclear weapons cause damage by way of blast, heat and radiation. Damage by chemical weapons is less severe, and biological agents are slow-acting. It is essential for military personnel to take protective measures when exposed to such kinds of warfare.

Effectively designed NBC suits are made for personal protective clothing. They provide protection against aerosol and droplets, and toxic vapours. This protective equipment works as a barrier against radioactive particles and heat flow which may come into contact with the skin.

In individual protection system/equipment, different elastomer-coated fabrics are utilised. A three-layer suit is designed to be used as an over-garment over the normal uniform. The outermost layer must have flame-retardant and oil-repellent polymer coating mixes on lighter weight Nylon fabric. The middle layer of the suit is fabricated from high-quality activated charcoal mixed with CR-based compound, coated in solution form on non-woven polyester fabric to absorb toxic gases if exposed to such environments. The innermost layer is lined with lightweight scrim from cotton fibre.

The suit is tailor-made and fitted with high quality plastic slide fasteners to slide open and close from the front. Suitable hook and loop (Velcro) tapes are used for proper closing of the suits, which are available in four sizes. It should have the property of breathability to reduce physiological stress. NBC suits are vacuum packed for long storage and to make it safe for transporting to theatres of war [23].

The decontamination suit protects the user against toxic gases and radioactive dust fallout. It is worn over normal garments by the soldier. It is impermeable, so it can be decontaminated and reused.

The outer layer of the decontamination suit is made from butyl rubber (usually bromobutyl) with flame-retardant additives incorporated in the rubber compounds. It is coated on lightweight Nylon fabric (usually olive green in colour). Coating is applied in solution form using a rubber spreading machine to obtain a thin impermeable coating on both sides of the fabric [24]. This suit is designed and tailored in universal size and can easily be worn over the military uniform. Photographs of an NBC suit and decontamination suit are shown in **Figure 6.24**.



**Figure 6.24** Protective clothing for NBC warfare. Reproduced with permission from European Army Surplus, UK

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# 7 Emerging Technologies in Polymer-coated Textiles: Smart, Intelligent and Nano-structured Fibres and Fabrics

**Dipak K. Setua**

## 7.1 Introduction

We are living in an age when considerable convergence has taken place between many fields of science and engineering which were otherwise separate or distinct. Emergence of new technologies in every field and their amalgamation has resulted in the development of smart and intelligent materials and systems. As a consequence, the structural complexity of materials has increased tremendously. The smallest division of materials and devices, which were previously known of as ‘micro-sized’, has reached to sub-micron and then to nano-states. Conventional materials have progressed from high-performance to functional then to smart and intelligent materials incorporating information science into the material structure.

The field of textiles and clothing, therefore, cannot remain aloof from the benefits of these new developments. We have always been inspired by nature to create our clothing to possess higher levels of function and smartness. The development of micro-fibres to mimic silk first and then to create finer and, in many ways, better fibres is an example of such efforts. However, most textiles and clothing up to the present time are generally lifeless. It would be useful to have clothing like our skin, which contains a layer of intelligent materials as sensors to detect pressure, pain, and temperature. Together with the brain, the skin can function intelligently to become responsive to environmental stimuli. It can generate large quantities of sweat to cool the body when exposed to heat, and can also increase blood circulation when it gets cold. Similarly, it changes colour when exposed to ultraviolet (UV) or other high-intensity radiations to protect us from intense skin damage or can be water vapour permeable, allowing moisture to penetrate but stop unwanted environmental species from getting in. The skin can shed, repair or regenerate itself. However, development of an intelligent material simulating our skin is a very challenging task. By using suitable coatings with chemicals, additives or polymers on textiles, coated textiles can be made impermeable to specific liquids, gases and fuels for use as speciality clothing, shelters, tents, liquid containers, and upholstery items. The purpose of applying a

protective coating of polymers on textiles is to achieve protection of the finished product primarily from water, weather, heat, flame, chemicals, gases, UV light and oils. The polymer coating provides adequate flexibility whereas the textile substrate contributes to the physical strength and dimensional stability of the coated textiles. Properly formulated polymeric coatings can protect the textile from the deterioration effect of microbial attack. There also remains the possibility to make them protective to nuclear, biological and chemical (NBC) species as well as resistant to thermal radiations. The parallel advancement of polymer science and textile technology has resulted in a phenomenal growth of coated fabrics, leading to the emergence of advanced technical textiles.

Technical textiles are redefining the boundaries of conventional textiles. They proved to be one of the most remunerative and fastest changing sectors in the global textile industry. They are superior to conventional textiles primarily for their technical performance rather than aesthetic or decorative purposes. They therefore offer value-added advantages to the growing range of downstream applications. Unlike conventional textiles, which are used traditionally for clothing and furnishing, technical textiles use a diverse range of raw materials, processes, products and vast areas of application to benefit of the non-textile sectors e.g., advertising, agriculture, construction, geo-textiles, automobile, shipping, railways, space textiles, packaging, defence, medical/hygiene, flooring, furniture, environmental protection and sports. For example, it is possible to develop by this technology a tyre-ply fabric with enhanced strength compared to conventional versions and yet with improved functional properties e.g., grip, rolling resistance. Gore-Tex is a bi-component membrane; the main part is made from expanded polytetrafluoroethylene (PTFE) combined with an oleophobic (oil-repelling) layer that protects the membrane from the natural oils that the human body produces, insect repellents, and cosmetics. The outer surface of the garment with Gore-Tex fabric is coated with a hydrophobic treatment which prevents wetting-out of the outer face, thus improving wet weather performance and improving breathability. The main applications of these membranes are in sportswear, where excellent water exchange is obtained with good elimination of sweat at the garment interface (breathability) and creation of an external barrier with excellent water repellence. Medical textiles and hosiery products with medicinal properties are rapidly expanding sectors of the technical textile sector. An important field of application of textiles in medicine is wound care (bandages and wound dressings). The medical textiles in such cases should have bio-compatibility, flexibility and strength, hydrophobicity, hydrophilicity, alcohol repellency, moisture regain, medicine-release capacity, and nanoporosity for moisture vapour-transmitting properties. They can be prefabricated as ready-to-use products. Apart from various bio-compatible skin-friendly fibres, some added functionalities need to be added during the production of the fibres or applied as a speciality finish that may include coating, or spraying padding

to the fibre, yarn, fabric or product. Similarly, technical textiles are also useful in the manufacturing processes such as production of filter fabric in the food industry and machine textiles in paper mills. Technical textiles are, therefore, beginning to replace conventional textiles and have better profitability, efficacy and potential for future growth of industrial sectors.

The term 'smart textile' is applied to conventional textiles coated with smart or intelligent materials, or generated as such from smart or intelligent polymer materials by various fibre-forming processes e.g., melt-, wet-, or electro-spinning techniques. The concept of smart materials was initially introduced in Japan in 1989 to describe a material with striking similarity to silk having a shape memory function. In the past two decades, classical textile and clothing industries have shifted their attention towards evolving smart textiles where more functions (e.g., protection for adverse climatic conditions, thermo-regulatory, safety, fashion or other conveniences) can be included over and above the purpose of clothing to enhance adaptability and efficiency for the user. Smart textiles represent the beginning of a new era in the world trade of textiles [1-3]. However, these endeavours have largely been based on the invention of new generation polymers such as shape memory/conductive/micro-encapsulated/stimuli sensitive/bio-compatible types, which are combined with successful evolution of technologies for converting them into fibres, fabrics and articles. Smart textiles can meet the demand of high value-added technology, allowing transformation of conventional industry into a competitive high-tech industry (i.e., from resource-based to knowledge-based technology). Choice of quality rather than quantity, scope of producing custom-made product, multiple usability with decontamination capability and above all excellent product services are envisaged.

## **7.2 Definition of Smart and Intelligent Textiles**

Smart textiles are materials which can integrate the functions of sensing, actuation, logic and control to respond to the environmental changes at the most optimum conditions in a useful and usually repetitive manner. They are evaluated in terms of changes in the material properties, geometry, mechanical or electromagnetic responses. Smartness describes the presence of self-adaptability, self-sensing, memory as well as multiple functionality and self-repairing characteristics in a material to withstand sudden changes. Intelligent textiles are smart textiles which have the additional quality of learning and adapting rather than simply responding to stimulus in a programmed manner. This is usually accomplished by the inclusion of an artificial neural network (ANN) into the smart structures, which works like a brain (i.e., with cognition, reasoning and activation capabilities).

The advanced and technical textiles used in aerospace engineering, structural and

transport industry, processing, medical sectors, and ultra-high-strength/fire-retardant/camouflage/breathable and antibacterial types are, according to the definition, not considered to be smart or intelligent textiles. However, they could also be converted to smart or intelligent varieties if multiple functions are incorporated to impart a broad range of uses for them.

### **7.3 Classification of Smart Textiles**

According to their response, smart textiles can be classified into following categories:

- (a) Passive smart: can sense only environmental conditions and stimuli.
  - (b) Active smart: sense and react to environmental conditions and stimuli.
  - (c) Very smart: can sense, react and adapt to environmental conditions and stimuli.
- (a) **Passive smart textiles** are the first generation of smart textiles, and can sense environmental conditions or stimuli. A wet cloth, after hanging freely in open air or under sunlight, takes time to dry in the usual passive way. An insulated blanket or a fire-fighting suit remains equally effective irrespective of the outside temperature or during a fire outbreak. Protective clothing of army personnel is another example of passive smart textile. A pH- or temperature sensitive sensor is used in association with an active fluorescent dye coated or embedded into the clothing through optical fibre technology (OFT) to achieve sensing and signal processing to effectively measure strain, temperature, displacement, pressure, electric or magnetic fields. These OFT-based sensors can trigger an alarm by changing their colours after detection of biological or chemical toxicants, electromagnetic or nuclear radiations, fire, explosives or other hazardous materials.
- (b) **Active smart textiles** are the second generation of smart textiles. They have sensors and actuators present together in the structure. The actuator acts by detecting signals directly or from a central control unit. The textiles can fine-tune their functionalities to specific agents or environments. For example, a breathable suit of army personnel allows sweat to evaporate but prevents rain droplets from penetrating into the clothing. Suits are manufactured using charcoal-impregnated non-woven textiles or active carbon sphere coated textiles which capture only chemical toxicants in their highly porous carbon layers but allow regular gases/air to pass through. Other examples of this category include textiles coated with shape memory polymers, micro-encapsulated phase-change materials (PCM), photosensitive polymers, and chameleonic textiles.
- (c) **Very smart textiles:** Very or ultra-smart textiles are the third generation of

smart textiles. They contain an ANN in association with a sensor and actuator of an active smart variety. Such textiles adapt their functionality to a changing environment automatically and provide professional help on demand on adaptation or counter response. The production of very smart textiles has become a reality by drawing on knowledge from several disciplines: materials science, electronic engineering, telecommunications, advanced processing technology, artificial intelligence, biotechnology, and medicine.

## **7.4 Functions of Smart Textiles**

Different types of functions in smart textiles have their designated role (although not all of them may be present simultaneously in each of the items). The functions may be envisaged as being due to the intrinsic property of the materials or incorporated while constructing a smart structure. They all should invariably be quite apparent and serve a useful purpose. The smart functions must be combined with a product without changing its basic performance requirements (e.g., a clothing outfit cannot be compromised in its desired comfort, manufacturing processes, wash ability or durability). Five types of functions can be realised in a smart textile, as described next:

- (a) **Sensors:** A sensor functions to collect a signal from a body or from the environment. For a lifeless object, it is easier to integrate a sensor in the object body connected directly to the source of energy supply. However, for a living object (e.g., human), the situation needs to process several types of bio-signals e.g., body temperature, acoustic (heart, lungs), ultrasound (fluid flow), motion (respiration, limb swing), humidity (sweat) and pressure (blood). Currently, the performance of a textile sensor faces some challenges, such as:
- Selection of the correct parameters for measuring various bodily functions and development of appropriate algorithms for the interpretation of the data obtained.
  - Inability to acquire of poor signals of relatively low amplitude.
  - Relatively brittle nature of the sensor causes problems due to changing contact with a wearer especially while in motion. This necessitates enhanced toughness, flexibility and stability of the materials used in its construction.
  - Short lifespan due to premature wear and tear as well as repeated laundering.
- (b) **Data processing** is an active function of textile sensors. They can provide a huge amount of data, but suffer from accuracy of their actual interpretation due to:
- Large variations of signals between wearers.



- Complexity in establishing interrelations between stationary and time-dependent signals.
- Availability of standard values and correlation parameters.

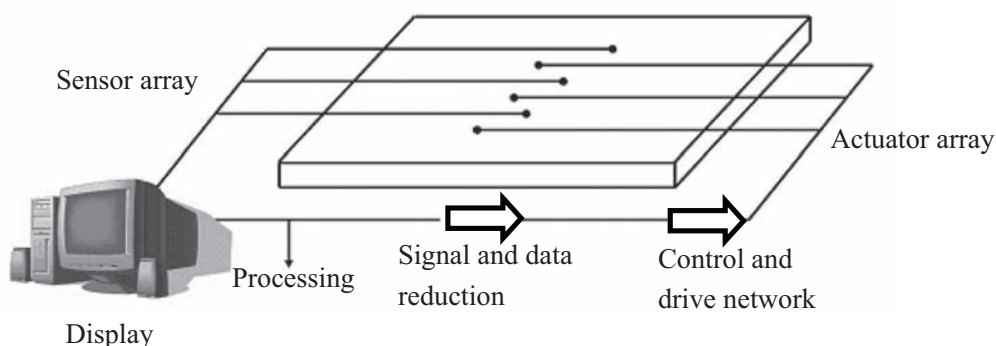
Furthermore, textile materials, having no computing power within them, require sophisticated electronics for signal conversion. Many practical problems e.g., fastness to washing, deformation and interconnectivity in the network for data processing, need to be overcome before real computing fibres are established in the marketplace.

- (c) **Actuation:** Actuators are meant for responding to an impulse produced by the sensors. After data processing, actuators can: make things move, result in changes of colours on exposure to light or change in temperatures, and make noise due to changes in electric or magnetic responses. These include the use of shape memory materials in the form of textile threads which react during a temperature change and which can be used as an actuator to smart textiles. Examples of other types of chemical actuators include specific substances which release a fragrance, skincare products, antimicrobial agents or drugs stored in microcapsules which are chemically bound to the textile fibre. However, active and controlled release of specific agents could be triggered only by changes in temperature, electrical or magnetic fields, pH, humidity, and use of chemicals as stimulants. Controlled release of drugs with a possible diagnosis could result in the development of intelligent components such as tapes and bandages.
- (d) **Communication:** An intelligent textile product, for example, a suit, requires communication with broader perspectives (e.g., connectivity within and between the individual elements from the wearer to the suit or from the suit to the wearer and the environment) to pass instructions. Within the suit, communication may be realised by the OFT or conductive yarns built seamlessly into the textile. For a driver, the vehicle should interact with the suit. A direct contact between the driver and the vehicle is possible through his suit and the seat on which he sits. Wireless connection can be achieved by integrating an antenna in the suit for a large surface area without inconvenience or action of the user. Such a prototype was reported by Philips Research Laboratories (UK) and Foster Miller (USA) at the *International Interactive Textiles for the Warrior Conference*, Boston, MA, USA, in 2002 [4–6].
- (e) **Data storage:** Functions such as sensing, data processing, actuation, and communication all require energy, mostly in the form of electrical power. Efficient management of energy therefore requires an appropriate balance of energy supply to storage capacity. Sources of energy, for example, for a garment, may be body heat, mechanical deformation of the fabric through body motion, exposure to

solar radiation, wind flow, or friction with the skin. Devices such as flexible batteries for energy supply as well as efficient energy storage have been reported by the researchers of Wollongong University, Australia [3]. However, in the case of a smart suit, the energy can be supplied through direct contact with the suit via a wireless connection. Micro-capsules can be used for storage of solids/liquids that can release latent heat energy by phase change on variation of environmental temperatures and subsequent migration of heat through the capsule body. An alternate source of instant power may be the use of smart dielectric elastomers in designing a heal strike generator or backpack suspension [7].

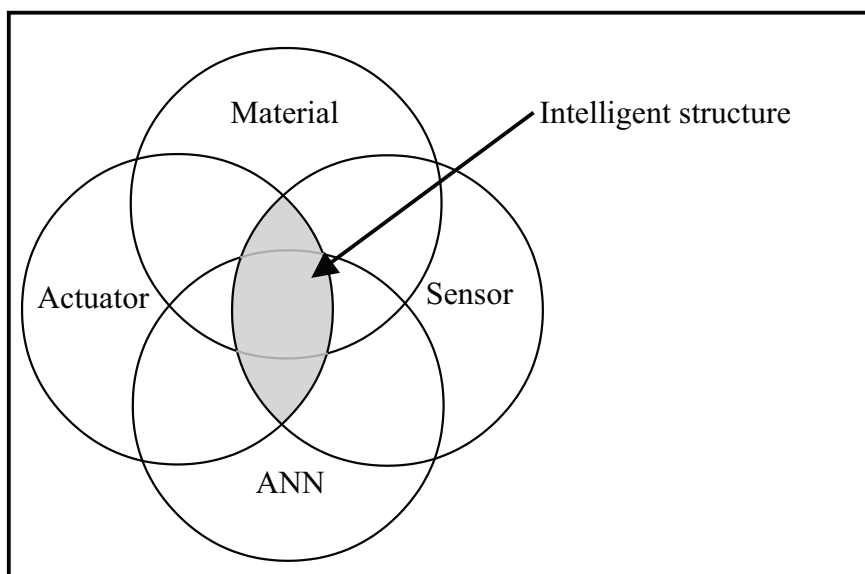
## 7.5 Configuration of Smart and Intelligent Structures

A smart structure (**Figure 7.1**) is a non-biological, physical structure that has a definite purpose, means and imperative to achieve that purpose with a biological pattern of functioning. Smart or adaptive structures are a class of advanced structures with integrated sensors, actuators and controls which allow adaptive change or response to external conditions.



**Figure 7.1** Configuration of a smart structure

An intelligent structure (**Figure 7.2**) is a smart structure that has the added capability of learning and adapting rather than simply responding in a programmed manner. This is usually accomplished by inclusion of an ANN into the structure.



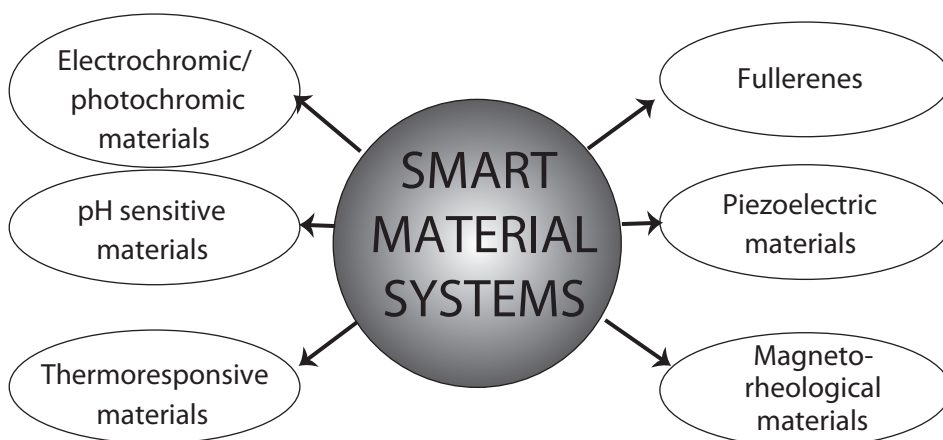
**Figure 7.2** Configuration of an intelligent structure

## **7.6 Properties of Smart Materials**

Materials science has undergone a distinct change from the development of advanced structural materials to functional materials and, recently, the emergence of intelligent materials. Smart or intelligent materials are materials which respond to environmental changes at the most optimum conditions, and manifest their functions according to these changes. Smart materials are not perfect systems but are used as part of a whole system, allowing development of higher grade systems with more accurate recognition, discrimination, and reaction capabilities. Variable properties which are manifested by smart materials are:

- Variations in surface colour or lustre of a fibre or cloth according to the intensity of the electromagnetic radiations falling upon them.
- Changes in the appearance due to variations of the extent or degree of load, creep, fatigue, or ageing time.
- Variations of the mechanical, thermo-physical, magnetic or electrical properties due to exposure to different surroundings and stimuli.

Comparison of the physical properties of smart materials with other conventional and high-performance materials is given in Table 7.1. Varieties of smart systems are depicted in Figure 7.3.



**Figure 7.3** Types of smart materials systems

Table 7.1 Comparison of smart and other conventional systems		
Category	Fundamental material characteristics	Fundamental system behaviours
Traditional materials, natural materials (stone, wood), fabricated materials (steel, aluminium)	Materials have given properties	Materials have no or limited intrinsic active response capability
High-performance materials polymers, composites	Material properties are designed for specific purposes	Have good performance properties
Smart materials	Properties are designed to respond intelligently to varying external conditions or stimuli	Smart materials have active responses to external stimuli, and can serve as sensors and actuators

Smart materials with variable structures or compositions can produce changes in the:

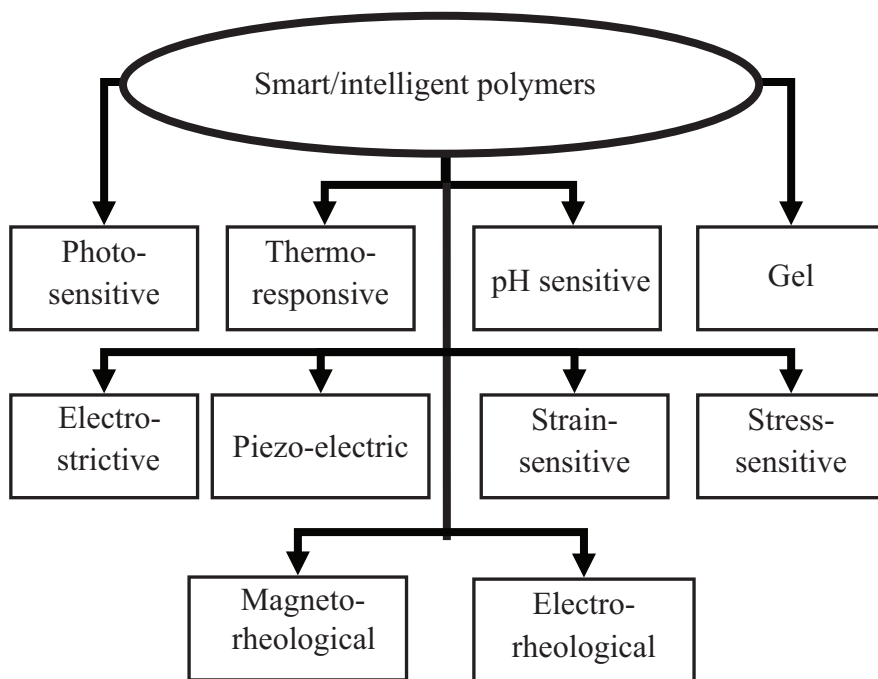
- Chemical composition according to surrounding conditions i.e., operating parameters, exposure to chemicals toxicants, damage due to radiation/corrosion,
- Variable functions due to phase transitions,
- Variation in electrical threshold according to the extent of applied load, type of signal, as well as the magneto- and electro-active properties of the material,
- Optical-threshold variations according to the amount of incident light and its frequency,
- Barrier properties of the material (which can also vary with a particular gas).

## **7.7 Varieties of Smart and Intelligent Polymers**

Smart and intelligent polymers can show distinct responses to differences in variations of the surrounding environment (e.g., thermal gradient, change in pH). Sometimes they are made intelligent by the way of harvesting their inherent properties in a wide range of applications [8]. In the simplest example, intelligent polymers are plastic strands that can carry electricity or alter their conductivity in response to stretching, heating, or incident sunlight. By weaving these strands into clothing outfits and measuring changes in the current passing through them, several new applications are possible. Various fascinating smart and intelligent polymers are shown in **Figure 7.4**.

## **7.8 Smart Polymers for Smart Textiles**

Challenges to mimic nature to develop clothing with higher levels of functionality and intelligence are quite obvious. Development of micro-fibres by starting from silk to creating finer, fashionable and comfortable fibres is ongoing worldwide. Among various smart materials, polymers appear to be the most promising for applications in the textile industry. Incorporation of these polymers in textiles would allow several functions to be combined in one place. This includes a change in surface gloss by altering the light-scattering coefficient, as well as incorporation of fibre sensors in the cloth to enable the measurement of temperature, stress-strain properties, and the presence of obnoxious gases and micro-organisms.



**Figure 7.4** Types of smart/intelligent polymers

Smart textiles represent the next generation of fibres, fabrics and articles produced to respond in time and can be described as textile materials that can ‘think and react’. These textiles are not confined to the clothing sector, but are important in the design of improved garments for protection, safety, fashion and convenience. Some prominent polymeric materials which are being used for construction of smart and intelligent textiles are classified as ‘microencapsulated phase-change materials’ (MPCM), ‘shape memory polymers’, ‘stimuli-responsive polymers’, ‘chromic materials’, ‘conductive materials’, and ‘electronics-incorporated textiles’.

### **7.8.1 Microencapsulated Phase Change Materials**

Microencapsulation involves enclosing micron sized particles of solids or droplets of liquids or gases in an inert shell, which in turn isolates and protects them from the external environment. The technology is mainly used for the protection and controlled

release of the core materials. The compatibility of the core material with the shell and the size of the core material has important roles for diffusion, permeability or controlled-release applications. Natural and manmade polymers provide the choice of shell material, which may be made permeable, semi-permeable or impermeable. Permeable shells are used for release applications, whereas semi-permeable or impermeable capsules are usually employed to protect the core material from the external environment (as well as to absorb substances from the environment and to release them again if brought into another medium). The morphology of the microcapsules is dependent upon the core material and deposition process of the shell. On the basis of their morphology, microcapsules can be classified as mononuclear, polynuclear, and matrix types. Mononuclear (core shell) microcapsules contain the shell around the core, whereas polynuclear capsules have many cores enclosed within the shell. In matrix encapsulation, the core material is distributed homogeneously into the shell material.

Assuming that the density of the core ( $\rho_c$ ) and shell ( $\rho_s$ ) materials are identical (i.e.,  $\rho_c = \rho_s$ ), it is possible to establish the relationship between the shell thickness ( $d_s = r_m - r_c$ ) and the ratio of the weight of the shell material ( $w_s$ ) to that of the core material ( $w_c$ ):

$$\frac{w_s}{w_c} = \frac{\frac{4}{3} \pi \left( \frac{r_m^3}{m} - \frac{r_c^3}{c} \right) \rho_s}{\frac{4}{3} \pi \frac{r_c^3}{c} \rho_s} \quad (7.1)$$

After rearranging, the following equation is obtained:

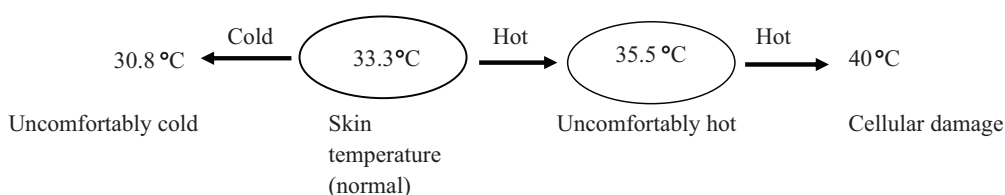
$$d_s = (r_m - r_c) = [\{w_s/w_c + 1\}^{1/3} - 1] r_c \quad (7.2)$$

**Equation 7.2** shows a linear relationship between the shell thickness and the capsule diameter if the ratio of  $w_c/(w_s+w_c)$  is in range 0.50 to 0.95 [9].

All materials store energy during heating ('sensible heat') and get warmer. During melting, the material changes from a solid phase to a liquid phase, and a large amount

of heat is stored at the melting point. The temperature does not change until all the material has melted. Hence, the energy stored in the material is called ‘latent’ heat (‘hidden heat’). During freezing, the material sets the latent heat free, and the amount of energy released at melting is called the ‘heat of fusion’ ( $\Delta H_m$ ). The important characteristic of latent heat is that it involves a transfer of a much larger ‘packet’ of energy than sensible heat. For example, 1 kg of water just below its boiling point needs to remove 4.2 kJ of energy to attain a temperature of zero degrees. To completely freeze the water, a further 330 kJ of energy needs to be removed. However, during the entire period of freezing, the temperature remains constant and the ice/water mixture co-exists. If heating the ice, it melts again, and the cooling of its environment can be used for air conditioning of an office building, for example.

The comfortable skin temperature of a human is 33.3 °C. If skin temperature drops to 30.8 °C, then the person feels uncomfortably cold. The same person, if moving to a hotter environment, feels uncomfortably hot if exposed to 35.5 °C. If the skin temperature rises to >35.5 °C, the level of perspiration increases so much that it might lead to a high level of discomfort if not managed appropriately. Once skin temperature, either locally or especially overall, reaches 40 °C, then there is the likelihood of cellular damage (Figure 7.5). All of these factors necessitate the skin to regulate its own temperature profile. This can be done using substances that undergo phase change within a temperature range just above and below the temperature of human skin. These materials, in general, are known as PCM. The property of these materials is harnessed in making thermoregulatory protective clothing for abruptly changing climatic conditions.



**Figure 7.5** Effect of environmental temperature on humans

‘Active wear’ means creating a ‘thermal balance’ between the heat generated by the body and that released to the environment. Conventional garments do not fulfill this requirement. The heat generated by the body during strenuous activity, such as in sports, is often not effectively released to the environment, resulting in a thermally



stressed condition of the wearer. Similarly, while remaining at rest in between different activities, less heat is generated by the human body and, considering the same heat release, hypothermia may occur. Fabric with MPCM incorporated, can be used to make clothing suitable for thermo regulatory protection. It can also provide a cooling effect to the wearer working above ambient temperature, acting as a 'heat sink' to absorb metabolic heat (which also serves to recharge PCM materials). The overall benefits obtained are a reduction in bulkiness (thickness) of the garment to provide more comfort, prevention of wetting from perspiration, and protection of the wearer for a longer time. Normal fire-retardant materials can also be used together with MPCM for development of fire-fighting suits.

#### ***7.8.1.1 Microencapsulation Technique and the Physical Properties of Microencapsulated Phase-change Materials***

Microencapsulation techniques are divided into two basic groups: chemical and physical. The latter is further subdivided into physico-chemical and physico-mechanical techniques. Various physical processes of the preparation of MPCM include coacervation, encapsulation by polyelectrolyte multilayers, polymer encapsulation by rapid expansion of supercritical fluids, coextrusion, and spray drying.

##### ***7.8.1.1.1 Coacervation***

Coacervation involves a phase-separation phenomenon. This is a partial desolvation of a homogeneous polymer solution into a polymer-rich phase (coacervate) and a polymer-depleted phase (coacervation medium). Two methods, simple coacervation and complex coacervation, are adopted. In the former, a desolvation agent is added for phase separation, whereas complex coacervation involves mixing two oppositely charged polymers in a solvent. There are three basic steps in complex coacervation: (i) preparation of the dispersion or emulsion; (ii) encapsulation of the core; and (iii) stabilisation of the encapsulated particle. First, the core material (usually an oil) is dispersed into a polymer solution (e.g., cationic aqueous polymer). In the second step, the polymer (anionic, water soluble) solution is added to the prepared dispersion. Deposition of the shell material onto the core particles occurs if the two polymers form a complex. This process is triggered by addition of a salt, changing the pH or temperature, or by dilution of the medium. The shell thickness can be controlled by addition of the second polymer. Finally, the prepared microcapsules are stabilised by crosslinking, desolvation or thermal treatment.

#### **7.8.1.1.2 Encapsulation by Polyelectrolyte Multilayers**

Polyelectrolyte multilayers consist of layer-by-layer electrostatic assembly of electrically charged particles. Core shell particles with tailored size and properties are prepared using colloidal particle as core material as well as a template upon which multilayers are fabricated. This technique allows formation of a controlled thickness of the multilayer film by varying the total number of layers deposited. Thus, the final properties of the capsules can be 'tuned'.

#### **7.8.1.1.3 Polymer Encapsulation by Rapid Expansion of Supercritical Fluids**

Supercritical fluids of carbon dioxide (CO<sub>2</sub>), alkanes (C<sub>2</sub> to C<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O) are highly compressed gasses. A small change in temperature or pressure can result in a large change in density of the supercritical fluids near the critical point. Supercritical CO<sub>2</sub> is widely used for its low critical temperature value in addition to its low toxicity, non-flammability, ready availability, high purity, as well as cost-effectiveness. It is also widely used in encapsulating active ingredients by polymers. Different types of core materials (e.g., pesticides, pigments, pharmaceutical ingredients, vitamins, flavours, dyes) are encapsulated using this method.

#### **7.8.1.1.4 Co-extrusion**

Co-extrusion is done by simultaneously pumping a dual fluid stream of liquid core and shell materials through concentric tubes, where they form droplets under the influence of vibration. The shell is then hardened by chemical crosslinking, cooling, or solvent evaporation. Different types of extrusion nozzles are used to optimise the process.

#### **7.8.1.1.5 Spray Drying**

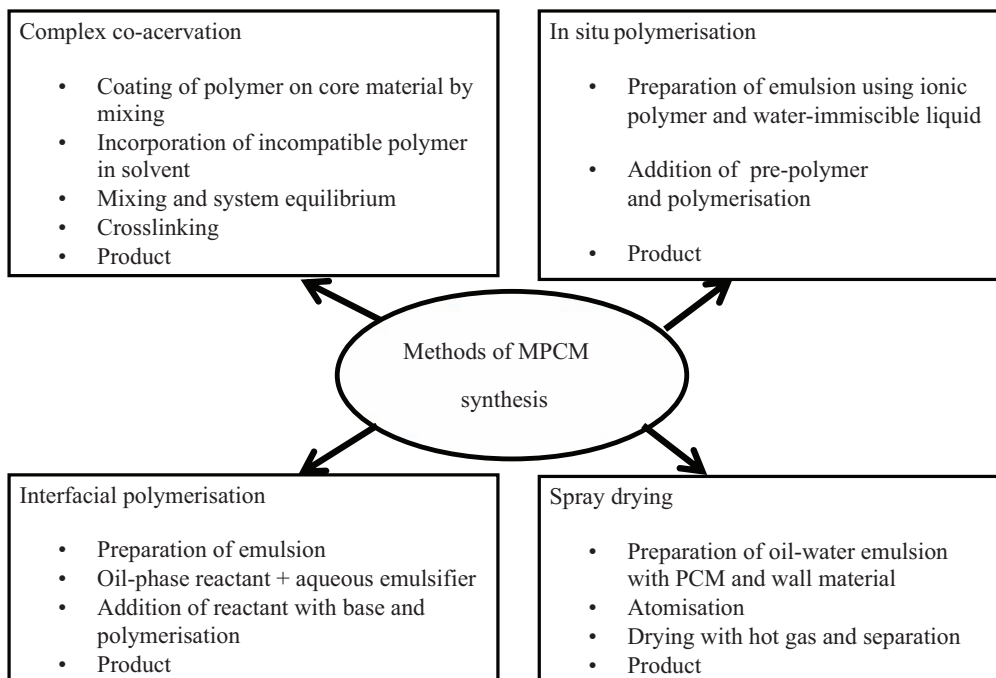
Microencapsulation by spray drying is a low cost commercial process which is mostly used for the encapsulation of fragrances, oils and flavours. Core particles are dispersed in a polymer solution and sprayed into a hot chamber when the shell material solidifies onto the core particles. As the solvent evaporates, microcapsules are obtained (which are generally of polynuclear or matrix types). Water soluble polymers are mainly used as shell materials because solvent-borne systems produce unpleasant odours and cause environmental pollution.

### 7.8.1.1.6 Chemical Techniques of Microencapsulation

There are two chemical techniques of microencapsulation: *in situ* and interfacial polycondensation. In the former, the solid core material is first dispersed in water containing urea, melamine or urea-formaldehyde condensate. An anionic polymer is added to assist formation of the amino-plast shell. In the next steps, formalin is added, the pH is adjusted to 2 to 4.5, and the mixture heated to 40-60 °C when shell formation takes place at the surface of the core material by polycondensation. Core material along with some multifunctional acid chloride and isocyanate are mixed together to form a water-insoluble mixture. The mixture is then dispersed in water with an emulsifier. Another reactant (e.g., multifunctional amine or alcohol) is added to the aqueous phase. Interfacial polymerisation occurs at the surface of the core, forming the shell to the microcapsule. Various methods of preparation of MPCM are shown in **Figure 7.6**. The particle sizes obtained in different microencapsulation processes are summarised in **Table 7.2**.

Table 7.2 Microencapsulation processes and range of particles sizes	
Micro-encapsulation types	Particle size (µm)
Co-extrusion	250-2500
Spray drying	5-5000
Co-acervation	2-1200
Solvent evaporation	0.5-1000
Phase separation	0.5-1000
<i>In situ</i> polymerisation	0.5-1100
Interfacial polymerisation	0.5-1000
Layer-by-layer assembly	0.02-20

MPCM are fine, free-flowing powders. Polyethylene glycol (PEG)-based MPCM-treated polyester, Nylon 66, cotton and wool fabrics are available which offer thermal storage and release properties 2-2.5-times greater than untreated fabrics, and which remain functionally constant even after 50 heating or cooling cycles. However, the main drawback of PEG-based MPCM is they are water soluble.



**Figure 7.6** Synthetic routes of preparation of MPCM (microcapsules containing PCM)

### **7.8.1.2 Applications of Paraffin Waxes in the Storage of Thermal Energy**

Paraffin waxes are saturated hydrocarbon mixtures of numerous alkenes. After refining, they become odourless, tasteless and non-toxic. For applications involving storage of thermal energy, paraffin waxes are encapsulated to form microcapsules and are integrated into fibres or are used as a coating on fibres or fabrics.

The benefits of using paraffinic PCM materials in clothing are:

- Capacity to absorb excess heat if the wearer is exposed to high temperature.
- Release of heat if the wearer feels cold.

- They greatly reduce the need for multiple layers of clothing as activity levels are varied.

A wide spectrum of PCM based on paraffin is available (Table 7.3) with widely different melting points for the purpose.

Table 7.3 Commercial paraffin available for PCM applications			
Serial Number	Compound name	Number of carbon atoms	Melting point (°C)
1	<i>n</i> -Octacosane	28	61.4
2	<i>n</i> -Heptacosane	27	59.0
3	<i>n</i> -Hexacosane	26	56.4
4	<i>n</i> -Pentacosane	25	53.7
5	<i>n</i> -Tetracosane	24	50.9
6	<i>n</i> -Tricosane	23	47.6
7	<i>n</i> -Docosane	22	44.4
8	<i>n</i> -Heneicosane	21	40.5
9	<i>n</i> -Eicosane	20	36.8
10	<i>n</i> -Nonadecane	19	32.1
11	<i>n</i> -Octadecane	18	28.2
12	<i>n</i> -Heptadecane	17	22.0
13	<i>n</i> -Hexadecane	16	18.2
14	<i>n</i> -Pentadecane	15	10.0
15	<i>n</i> -Tetradecane	14	5.9
16	<i>n</i> -Tridecane	13	-5.5

A novel way to improve the thermal insulation of paratrooper clothing is by using MPCM exposed to solar radiation. The increase in temperature of the clothing is interrupted at the melting point of the PCM due to absorption of latent heat. Conversely, in the cooling process at low ambient temperature, a drop in skin temperature is prevented by the solidification of PCM. To enhance the capacity of fabrics with MPCM incorporated in them, and to ensure that they can work for a longer period of time with better efficiency, the following methods are adopted during the synthesis and processing of MPCM:

- Size of the MPCM is maintained in the range of 5-20  $\mu\text{m}$  with 80-85% loading of PCM.
- A mixture of PCM with different transition temperatures (28-35  $^{\circ}\text{C}$ ) can be encapsulated together in a same outer shell polymer so that transitions can be effective over an extended period of time.
- More than one layer of MPCM can be used with increasing or decreasing transition temperatures (28-35  $^{\circ}\text{C}$ ) moving away from the skin surface with appropriate optimised insulation thickness. Hence, the rate of heat absorption in the composite fabric will remain relatively constant until the multiple layers of MPCM are exhausted.

#### ***7.8.1.3 Method of Incorporation and Functioning of Microencapsulated Phase-change Materials in Textiles***

MPCM are used for the manufacture of temperature regulating textiles at the fibre stage or as a coating in non-woven (**Figure 7.7**), woven or a knitted fabric. These microcapsules are embedded in the strands of synthetic fibres or embodied in the layer of a fabric. If the PCM reaches its melt temperature, it begins to change into a liquid within the supporting structure. The combined influence of capillary forces of the supporting structure and the special crosslinked additives ensure that the PCM (even if in the liquid phase) does not leak out of the structure [10]. Therefore, one always works with a dry material and liquid handling problems are eliminated. Free spaces within the bound MPCM allow volume expansion of the PCM to take place within the structure and so are not apparent. These materials are enclosed in a protective envelope, so they are not affected by laundering, cleaning and other kinds of environmental exposure of the protective garment [11].

Incorporation of MPCM in individual fibres (**Figure 7.8**) can be achieved by solution blending of the microcapsules with the polymer, and spinning the composite fibre by wet- or dry-jet wet spinning processes. The microcapsules in this case are embedded inside the fibres, which prevent the loss of microcapsules due to bursting.

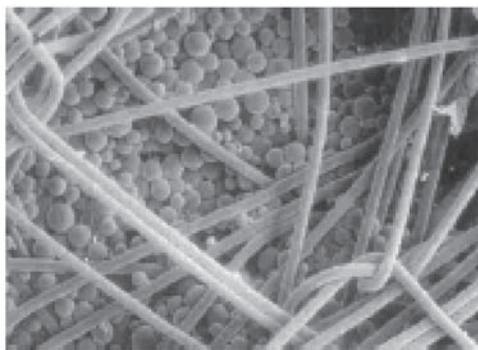


Figure 7.7 Entrapment of microcapsules in a non-woven fabric.

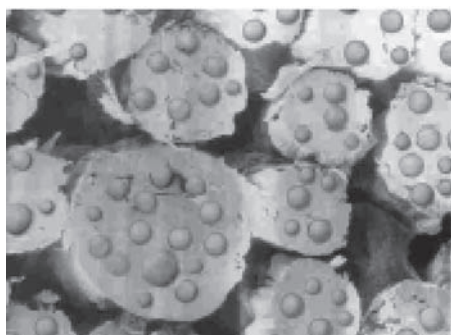
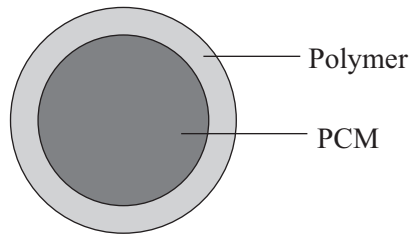
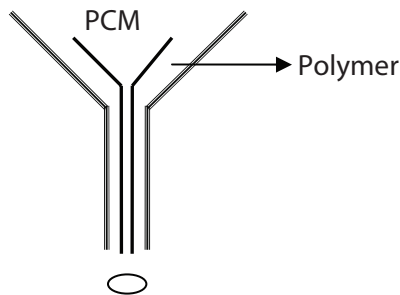


Figure 7.8 Incorporation of PCM microcapsules in fibres

Bi-component extrusion is a spinning technique used to simultaneously extrude two different polymers through the same orifice by dry or melt spinning techniques. This produces fibres mainly with a combined core and top sheath components (although matrix-fibril and other structures are possible). The process incorporates the MPCM materials inside the core of a fibre whereby the core consists of a PCM material and the sheath comprises a polymer-like polyethylene (PE), polypropylene (PP), Nylon, or polyacrylonitrile (Figures 7.9 and 7.10).



**Figure 7.9** Fibre cross-section



**Figure 7.10** Spinneret assembly

MPCM microcapsules can also be incorporated in foam [12]. The foaming technology enables a significantly higher amount of microcapsules to be incorporated.

#### **7.8.1.4 Commercial Varieties of Microencapsulated Phase-change Materials**

Outlast (Boulder, CO, USA) produce MPCM which, as a coating, can be incorporated into non-woven or adhesively bonded with the fabric structure [13-15]. Outlast's temperature regulating fabrics from Gateway Technologies Inc., (Boulder, CO, USA) use a cyclic process to absorb, store or release heat to maintain comfortable temperature equilibrium within the microclimate condition between the fabric and the skin [16]. One variety of MPCM, developed by the firm, has an insulation performance 400% higher than that of conventional lofted insulation materials.



Microtek Laboratories Inc., (Dayton, OH, USA) has produced MPCM 43-D, which shows a phase change at 43 °C [17]. Other MPCM have melting points between -30 °C to 55 °C. A primary use of MPCM products is in the coating of fabrics and foams for textile industries. These are used in various types of apparel such as inner and outer garments, gloves and footwear. PCM 72 from Merck can store four times more heat than water and ten times more heat than stone or brick in the temperature range 70-80 °C [18]. Rubitherm GmbH have produced 'bound PCM' developed by Dayton Research Institute (Dayton, OH, USA). In their PCM, paraffin waxes are encapsulated within a secondary supporting structure by means of special additives, which are defined by the particular end-use applications. This provides a matrix in which the PCM is homogeneously distributed so that neither the additive nor the supporting structure changes the crystalline structure of the PCM to avoid loss of heat during storage. In general, Rubitherm PCM are available in powder or granular forms, and work in the temperature range 50 °C to 110 °C.

### **7.8.2 Shape Memory Polymers**

Shape memory polymers (SMP) are stimuli responsive materials that can recover their original shape from large deformation even after extended period of applications. External stimuli such as heat, light, electric fields or magnetic fields are used to trigger the shape changes of SMP. These materials comprise two phases: fixing phase (which remembers the initial shape) and permanent phase (which can be attained reversibly due to exceeding the transition temperatures of its soft and rigid segments on exposure to these stimuli). The basic advantage of SMP over other shape-memory materials (e.g., metals or ceramics) is their inherent characteristics of high recoverable strain of several hundred percent and much lower specific density [19].

Particular types of multiblock copolymers of segmented polyurethane (SMPU), which show a thermally induced shape-memory effect, have become commercially important. In sharp contrast to shape-memory metals such as 'Nitinol', they are cheap, lightweight and can withstand large recoverable strains up to 100%. The drawback for shape-memory metallic alloys is 'programming' them (see next) for shape-memory applications by a heat treatment process carried out at temperatures of several hundred degrees because this is a time consuming procedure. The maximum deformation that they can undergo is only ~8%, and they are much more expensive than polymers. One component, oligo(ε-caprolactone) dimethacrylate, furnishes the crystallisable 'switching' segment that determines the temporary and permanent shape of the polymer. By varying the amount of the co-monomer, *n*-butyl acrylate, in the polymer network, the crosslink density can be adjusted. Hence, the mechanical strength and transition temperature of the polymers can be tailored over a wide range. The shape-memory behaviour can be produced with an appropriate

combination of structure and morphology with significantly different chemical compositions. Most of the shape-memory effects are based on the separate phases that will go back to the coiled polymeric structure, crosslinks, and hydrogen bonding. The shape-memory transformation is dependent upon the mechanism by which polymer molecules transpose between the constrained to random coiled formations. In SMPU, microcrystals (hard segment) are used for memorising the original shape, and the rubbery state (soft segment) is used to maintain the transient shape (it absorbs the external stress applied to the polymer). A high degree of elastic recovery of the soft segment at room temperature and the formation of a stable hard segment domain acting as physical crosslinking are the necessary conditions for reversible shape-memory behaviour which are available with SMPU thermoplastic rubber [20, 21].

The mechanism of the shape-memory effect is based on thermally induced phase-separated morphology with one phase acting as a 'molecular switch'. If the temperature is higher than the glass transition temperature ( $T_g$ ) or melting temperature ( $T_m$ ) of the polymer, the segments become flexible and the polymer can be deformed elastically. The temporary shape is established by cooling down below the  $T_g$  or  $T_m$ . If the polymer is heated up again, the polymer reverts to the permanent shape. Deforming a polymer system to its temporary shape is called 'programming', which includes cold drawing and heating. A permanent shape can, therefore, be stored while the alternative shapes are temporarily induced. The phase responsible for the highest thermal transition, such as the highest  $T_m$  among all the phases, is the basis for the permanent shape. Above this temperature, the polymer is completely in the molten state. The  $T_g$  can be used as a molecular switch for a temporary shape.

In recent years, a considerable amount of research has been carried out in the development of polyurethane-clay nanocomposites for their large increases in the property spectrum (e.g., thermal stability, gas barrier properties, tensile properties) as compared with pure polyurethane. They should be of potential use for smart and comfortable military garments. Because of their elastic memory effect and response at the molecular level, they can be used as polymer coatings to open-up their structure if the wearer becomes overheated, allowing body heat and sweat to escape. If the atmosphere is cold, the molecular structure closes to prevent the loss of metabolic heat to the environment, thereby keeping the body warm [22-24]. Other possible applications are biodegradable catheters, sutures, stents and orthodontic wires, as well as pliant guidewires, and tools for bloodless surgery.

### **7.8.3 Stimuli-sensitive Polymers**

Intelligent, responsive fibres based on stimuli sensitive polymers (SSP) can reversibly change structure and properties in response to external stimuli (e.g., temperature, pH,

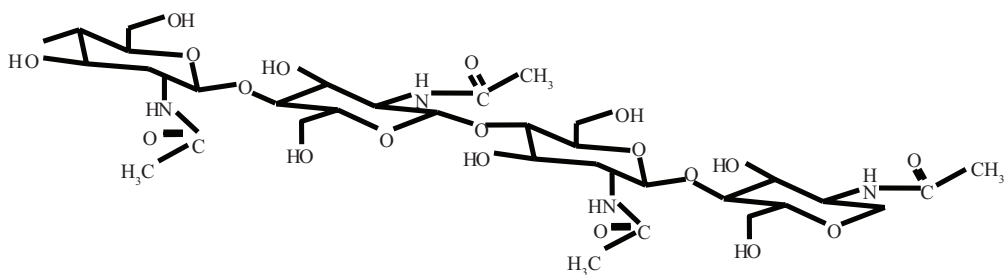
ionic concentration) [25, 26]. Stimuli-sensitive fibres and fabrics can be developed by the grafting or coating of conventional fibres or fabrics, or can be generated into these products entirely from SSP by melt spinning, solution spinning, or electro-spinning techniques (e.g., polyacrylic acid (pH-responsive polymer) and poly(*N*-isopropyl acrylamide (PNIPAAm), a temperature responsive polymer). From such materials, gas sensors can be developed to estimate the concentrations of CO<sub>2</sub>, nitrogen dioxide (NO<sub>2</sub>), and sulfur dioxide (SO<sub>2</sub>) in the atmosphere [27, 28]. Bandages can be developed with temperature sensitive polymers which can be wrapped loosely on the wound, but which shrink and wrap hard if experiencing an increase in body temperature. The bandage can be cooled below its transition temperature to be loosened and removed without harming the wound. By coating them on the surface of the fabrics, temperature sensitive polymers can also be used for controlling the permeability at different temperatures.

Hydrogels are polymer networks that do not dissolve in water but which swell or collapse in changing aqueous environments. They are useful in biotechnology for phase separation because they are reusable and recyclable. PNIPAAm is a temperature sensitive polymer which has a low critical solution temperature of ~32 °C and which exhibits a significant (but reversible) hydration-dehydration change in response to temperature that is close to body temperature. In particular, PNIPAAm hydrogel has been widely applied to temperature sensitive drug delivery systems, separation membranes, and tissue engineering scaffolds. Many attempts have been made to graft the surface of PNIPAAm-*g*-PP non-woven fabrics to develop novel temperature sensitive smart fabrics that are reversible in response to changes in water vapour permeability. A comprehensive review of the application of temperature sensitive hydrogels to textiles has been published by Liu and Hu [29]. The authors described the possibility of grafting of *N*-isopropyl acrylamide (NIPAAm) onto the surface of cotton fibres using the <sup>60</sup>Co irradiation method and photografting of acrylic acid (AA) onto fibrous carboxymethyl cellulose in the presence of *N,N*-methylenebisacrylamide as a crosslinking agent for use as smart fabrics with temperature sensitive water absorbance. To create a dual temperature/pH-sensitive hydrogel-grafted fabric, a vinyl-capped polyurethane ionomer was grafted onto the non-woven cotton cellulose together with NIPAAm by random copolymerisation initiated by ammonium persulfate. Apart from temperature sensitivity close to body temperature, the grafted cotton cellulose has pH sensitivity. The temperature/pH dual-sensitive hydrogel has great potential application in smart fabrics.

#### ***7.8.3.1 Smart Textile Materials with Biopolymeric Systems***

Various polymers (synthetic and natural) are available for surface modification of fibres, fabrics and textiles. However, due to environmental concerns, increasing

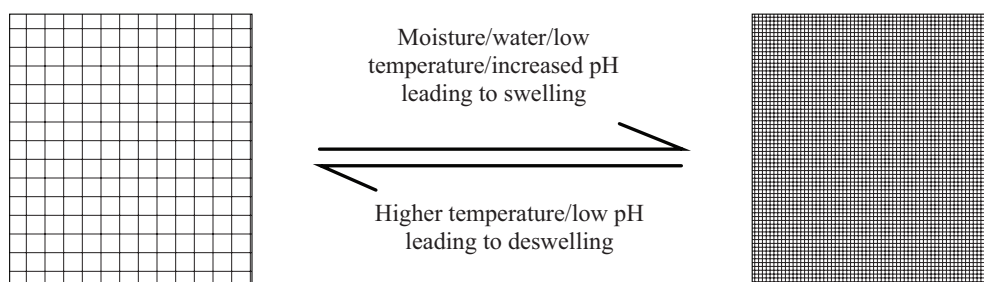
impetus is given to the usage of biopolymers. Among the different types of biopolymers, polysaccharides of animal origin such as chitin (and its derivative chitosan) are receiving a great deal of interest. The structure of chitin (**Figure 7.11**) is similar to that of cellulose (*N*-acetyl glucosamine replacing glucose). Chitosan is the *N*-deacetylated derivative of chitin.



**Figure 7.11** Molecular structure of chitin

Chitosan shows biocompatibility, biodegradability, anti-bacterial properties, non-toxicity, excellent adsorption behaviour, and may also be coated on cotton. It is available in film, microgel, hydrogel, fibre and also as blends with different biodegradable polymers of special interest (e.g., polyvinyl acetate, polyacrylic acid). The application of chitosan-based, pH-, temperature- and temperature/pH dual-sensitive hydrogels is of special interest. Chitosan-based hydrogels can be stabilised by various chemical and physical crosslinking, and their absorbing capacity can be greatly improved by the presence of synthetic polymers such as polyacrylate. Gels obtained by self-curing of chitosan with AA and methyl acrylate absorb up to 500 times their dry weight and can therefore be classified as ‘super-absorbents’. A hydrogel of a mixed nature based on a copolymer made of chitosan with different degrees of polyacrylamide shows swelling equilibrium 300-3,000 times the volume of the dry solid polymer in different media while preserving its integrity and strength [30]. All these gels could be attached to textile substrates and even a very small change of stimulus (e.g., 1 °C change in temperature) could make a certain gel swell or collapse hundreds of times in volume. By attaching these gels as surface-modifying systems to textile substrates, their ‘smart’ properties could be readily transmitted to textile materials and new advanced materials created. The amino group of chitosan (which is

rare in polysaccharides) could be functionalised using NIPAAm molecules for grafting. Introduction of PNIPAAm to the chitosan chain improves its moisture absorption and swelling behaviour, which is sensitive to pH, temperature and moisture content [29]. The fibres which are made using PNIPAAm-grafted chitosan have the potential to be converted into smart fabrics (**Figure 7.12**) in the pristine form or in blends with other synthetic fibres or natural fibres. The stepwise swelling/deswelling behaviour confirmed that the process is repeatable in accordance with the changes in moisture, temperature and pH. This shows that this material could be used for the production of a new class of stimuli sensitive fibres or fabrics [31].



**Figure 7.12** Chitosan/PNIPAAm fabrics

Stimuli-sensitive (especially pH-sensitive) fibres could also be produced from polyvinyl alcohol/polyacrylic acid copolymers to demonstrate pH-sensitive swelling behaviour [32].

#### **7.8.4 Chromic Textiles**

Other types of smart or intelligent textiles are those that change their colour reversibly according to external environmental conditions. Hence, they are also called ‘chameleon fibres’. Chromic materials, in general terms, refer to materials that radiate the colour, erase the colour or change it because of induction caused by external stimuli. They can be classified depending on the type of stimuli. Out of an extended list of chromic materials, the types described next are particularly important for coated textiles.

#### **7.8.4.1 Photochromic Textiles**

Smart materials that respond to light are called ‘photosensitive materials’ and the phenomenon of colour change of light on exposure to photonic radiation is called ‘photochromism’. Like photochromic dyes, photosensitive polymers (which are generally p-conjugated polymers) can also interact with the electromagnetic radiation in the long UV (300-400 nm), visible (400-700 nm) and near infrared (IR; 700-1500 nm) ranges to produce various effects, which are reversible if the radiation is withdrawn. Photochromism is of two types: positive and negative. In the former, the colourless substance becomes coloured if exposed to light due to a unimolecular reaction. In the case of negative photochromism, the conversion is from coloured to colourless by a bimolecular reaction. Such transformation between two electronic states of materials is possible but the process, although non-destructive itself, may be subject to side reactions caused by solvents and oxidation. Inorganic photochromic dyes are, in general, very costly in their purest form, sensitive to environmental conditions (particularly moisture) and involve many critical technologies in their development and purification. Fibres with these materials emit fluorescent colours (e.g., blue, green, red) under UV radiation in a dark place and which revert back to their original colour when exposed to natural sunlight. The inorganic fluorescent paints used for this purpose are mixed at an approximate weight of 10% in the liquid during the fibre-spinning process.

The technological advantages for the production of coated or finished fibres or fabrics with polymers have three main advantages over inorganic-based materials: (i) reduction of cost by large-scale production; (ii) the possibility of producing large area flexible devices; and (iii) tunability of the electronic band gap by regulation of the chemical synthesis. Conjugated polymers have been investigated for a wide range of novel applications, such as organic light-emitting diodes, thin-film transistors, solar cells, photo-sensors and chemo-sensors. However, these materials, in general, do not show photochromism in the crystal form. Melting or dissolution in certain solvents significantly changes their behaviour (colour emission, reaction speed variation, resistance, density). Hence, when applying these materials to fibres, it is important to consider the correct type of solvent. Examples of some potential photonic p-conjugated polymers are polyacetylenes, poly(*p*-phenylenevinylenes), poly(*p*-phenyleneethylene), polythiophenes (PT) and poly(3-alkylthiophenes). The greater interest in the latter arises from inserting a suitable substitution in the phenylene rings of the backbone of PT, thereby converting them into long flexible side chains generating good processability and improved photoluminescence efficiency. These polymers are highly selective and sensitive to external stimuli due to the intrinsic nature and presence of well-defined structures [33]. The response, however, is largely dependent upon the particular wavelength (excitation energy) of the light source. The efficiency of the fluorescent properties of the polymers is also dependent upon: (i) solubility in common

low-volatile solvents; (ii) film-forming properties to obtain continuous thin-film (the thinner the film the higher is the efficiency); (iii) ion mobility or transport properties; (iv) chain length of the conducting polymer.

An approach to enhance the fluorescence signal intensity and sensitivity of the conjugate polymers has been described as ‘amplification’ and the polymers possessing such amplification are called ‘amplifying fluorescent polymers’. These fluorescent polymer molecules (which are joined in a molecular chain in series) show high sensitivity, fast responses together with high-intensity amplification in the presence of light [34-36]. Smart photosensitive fibres and fibre-based smart products are considered to be an exciting area of textile development. In defense applications, these materials have tremendous potential because they will be useful in the design of interactive electronic textiles, electric blankets and sweaters, and fabrics with ‘auto camouflage’ [37]. Photosensitive polymers can be incorporated in the fabric or in the fibre. On excitation with photons of characteristic wavelength, the amplification could produce electricity that can be stored and used in electronic devices used by military personnel. Polymer-coated fibres can be prepared by a conventional fibre-spinning method (melt processing or solution processing) or electrospinning. If applied to fabrics as coatings or finishes, they can store light and can be used in working clothes for use in darkness.

#### **7.8.4.2 Thermochromic Textiles**

Reversible colour change can also happen with thermochromic textiles, and this phenomenon is called ‘thermochromism’. Most thermochromic materials are not suitable because the significant change in colour requires a large amount of heat to induce intermolecular transformation. A liquid system is usually used to achieve a significant change in appearance over a narrow temperature range of 5-15 °C and also to detect small variation of temperatures (e.g.,  $\leq 1$  °C). Two types of thermochromic dyes commonly used in textiles are the liquid crystal type (cholesteric type) and the molecular rearrangement type. In both cases, the dyes are entrapped in microcapsules and applied to garment fabrics in a resin binder. Thermochromism results from selective reflection of light by liquid crystals, and the wavelength of reflected light is characteristic of the refractive index. The latter varies with temperature, as does the colour of the reflected light emanating from the coated fabric. An alternative means of inducing thermochromism is by rearrangement of the molecular structure of a dye (e.g., spirolactones). A colourless dye precursor and a colour developer are dissolved in an organic solvent. The solution is then microencapsulated and is solid at lower temperatures. Upon heating, the system becomes coloured or loses its colour at the  $T_m$  of the mixture. The reverse change also occurs at the same temperature if the mixture is frozen. Toray Industries (Tokyo, Japan), reported on the development of



a temperature sensitive fabric made by introducing microcapsules of glass spheres (diameter 3-4 mm with enclosed heat-sensitive dyestuff) which are resin-coated over the fabric surface. The chromophoric dyes (electron acceptors) and colour neutraliser (alcohol) exhibit colour changes according to the environmental temperature. Sway® made by Toray Industries are multicolour fabrics which reversibly change colour at temperatures  $>5^{\circ}\text{C}$  and are operable from  $-40^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ . The change of colour with temperature of these fabrics is designed to match various applications (e.g., for skiwear  $11-19^{\circ}\text{C}$ ; women's clothing  $13-22^{\circ}\text{C}$ ; and temperature shades  $24-32^{\circ}\text{C}$ ).

#### **7.8.4.3 Ionochromic Textiles**

Ionochromic dyes are sensitive to pH and examples include phthalides, triarylmethanes and fluorans. They are directly thermally printed onto textile substrates containing an acid co-reactant in a single layer. By heating the surface, the components react themselves and produce a colour.

#### **7.8.4.4 Solvatochromic Textiles**

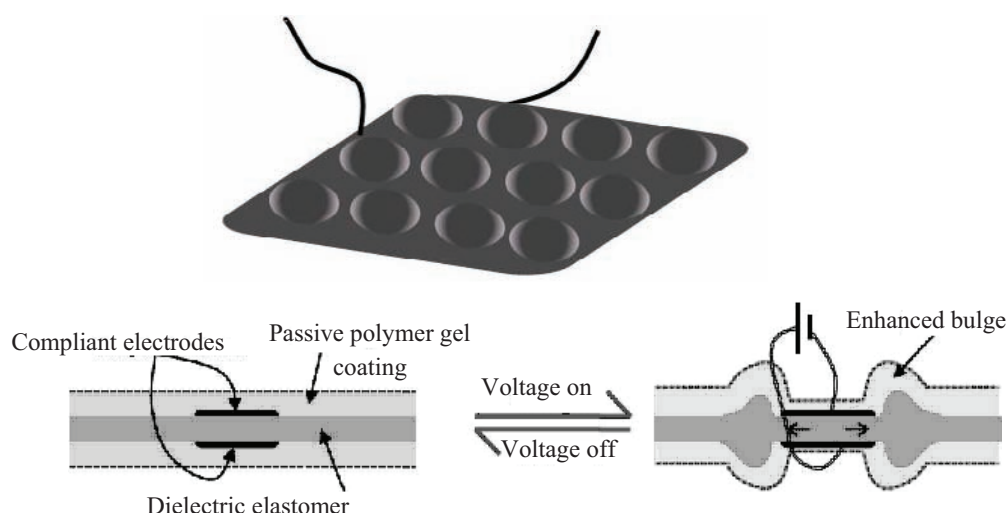
Some of the fibres exhibit solvatochromism (colour change if they come into contact with a solvent or water). These materials are used for the construction of swimsuits as well as garments for fashion designs whereby the colour changes accordingly with the volume of incident light.

#### **7.8.5 Electroactive Polymers**

Of particular significance amongst the electroactive polymers (EAP), dielectric elastomers are showing great potential. They can demonstrate large strain, fast response and high efficiency, suggesting wide applicability. Interest in the dielectric elastomer actuator (DEA) has encouraged the search for the best materials with high dielectric constants and breakdown voltages, good mechanical properties, and resistance to harsh environmental conditions. Most of the literature on the DEA has reported on the use of commercial materials such as VHB 4910 from 3M (St. Paul, MN, USA), the silicone elastomers Sylgard 184 from Dow Corning (Midland, MI, USA) and Elastosil from Wacker (Kolkata, India) [7]. The DEA is a three component system consisting of a soft dielectric elastomer between two compliant electrodes. Application of an electric field polarises the elastomer, generating stress within the material known as 'Maxwell' stress. Coulomb forces arise between the oppositely charged electrodes, the actuator stretches in the direction perpendicular to the force and thins down in the parallel direction of the force. Electrodes have traditionally



been constructed from a mixture of conducting particles, grease or curable elastomers, which allow brushing of fine conducting powder on sticky dielectric elastomers. Dielectric elastomers can be used for intelligent textiles that change their surface quality (Figure 7.13), with compliant electrodes spaced as dots over and under the dielectric elastomer. After application of an electric field, the elastomer changes its thickness between electrodes, which results in bulging on the fabric surface. The effect of bulging can be more predominant if it is made of a soft polymeric gel. Such intelligent surfaces can be used as stealth and camouflage clothing, as well as in pressure suits for pilots of fast jets [38].



**Figure 7.13** Intelligent textile coated with a dielectric elastomer

### **7.8.6 Conductive Fabrics**

Conductive fabrics combine a high wicking type of finish with high metallic content (e.g., addition of nickel-, copper- and silver-based coatings of varying thickness). These fibres can provide a combination of enhanced physical and electrical properties (e.g., a 1,000-fold increase in thermal conductivity over conventional polymer-coated clothing for various demanding applications) [39]. Their usages cover development of sports apparel with negligible thermal insulation but enhanced wearing comfort. Different

trademarks of products can offer various advantages: they are lightweight, flexible, durable, cost-competitive and, above all, can be crimped, soldered and subjected to conventional textile processing operations.

#### ***7.8.6.1 Development of Electromagnetic Shielding Apparels***

In recent years, the use of electrical and electronic devices has grown rapidly. Many devices such as computers, printers, modems, AC motors, calculators, electronic home appliances, and cellular phones can emit a radiofrequency signal. There is a worldwide concern about the potential health hazards (cancer) that could be associated with exposure to these electromagnetic radiation. Design and development of suitable garments to shield electromagnetic energies have become, therefore, a necessity. Traditionally, metals and alloys used for this purpose are heavy and non-flexible. Conductive textiles have started replacing metals for various shielding applications. The cathode sputtering method for manufacturing ultra-thin metallic coatings on textile products for making screening materials in the shape of wallpaper has been reported [40]. Magnetic fibres for designing textile magnetic elements which can be used to monitor selected human physiological parameters are now available [41]. Standardisation and measurement methods for the screening effectiveness of conducting textile materials have been described by Wieckowski and Janukiewicz [42].

For protecting people from direct exposure of electromagnetic radiation, the shielding material should be wearable in the form of conductive textile fabrics for protective wear for: protection of pregnant women, users of computers and microwave ovens, workers in television and radio stations, hospitals, and patients with implanted electronic materials. Conductive textile fabrics with desirable electromagnetic shielding effectiveness and mechanical properties can be developed from core-spun or intimate blended yarns. In core-sheath type yarns, the metallic filaments are in the core, and normal textile fibres (cotton, polyester and viscose) are in the sheath. The very fine metallic filaments will ensure a lower fabric weight and high flexibility. Intimate blended yarns can be developed from very fine stainless-steel staple fibres and other normal textile fibres (cotton, polyester or viscose). About 5–20% of very fine staple stainless steel fibres are blended with normal fibres at the spinning stage to obtain blended yarns. Single and two-ply yarns can be used to develop woven/knitted fabrics by varying the constructional parameters: ends and picks per inch, loop length, and loop density [43, 44].

These materials also offer new opportunities to designers in developing portable products that are flexible, user-friendly for man/machine interactions, and also provide scope for the development of novel types of sensory fabrics. Position sensing (i.e., capability of reading the location in fabric) and pressure sensing (e.g., finger

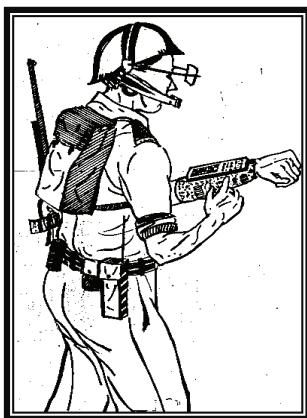
press) systems can be produced from conductive fabrics. It is also possible to create lightweight switching and sensing technology that can conform to three-dimensional (3D) shapes which is durable, cost-effective, washable, wearable, and desirable. Pressure readings can be obtained from smart fabrics which allow the user to differentiate between inputs ranging from high-speed impact to gentle strokes, and these features can be incorporated into textiles without significantly increasing their cost or compromising end-use properties [45-48].

Another application of conductive fabrics is in the development of clothes for extreme winter conditions or diving suits. In these cases, an external heat source produces energy which is conducted uniformly by the conductive fabric to distribute the heat throughout the entire garment/suit and the body. Another interesting application is a heated car seat, where in traditional systems a substantial amount of extra padding is used. The thick foam pad acts as a thermal insulator, effectively holding the heat from the heating wire down into the seat foam rather than transferring it to the driver. An inherently conductive material, therefore, provides an advantage over the existing wire system to achieve uniform distribution of temperature. This is non-hazardous, eliminates problems of wire breakage, and is cost-effective.

### **7.8.7 Smart Clothing with Electronic Devices**

The new generation of integrated intelligent textiles for clothing is an exciting new field which combines the innovative ability of the clothing industry to meet market demands and integration of smart features into classical products. With revolutionary advances occurring at an unprecedented rate in science and electronics, the possibilities offered by wearable technologies have huge potential for future business sectors. Clothing represents the ideal interface between the human with his/her surrounding environment. Everybody wears clothes in several layers one above the other routinely in different climatic as well as various day-to-day situations. As the technologies become increasingly refined, complex systems and several micro-components can be embedded unobtrusively in clothing, thereby enabling a human to be 'communicative' with his/her environment.

This field of innovation, in commercial terms, is gradually developing into high-tech products, especially in military applications. Smart clothes define intelligent clothing in combination with mobile multimedia with wireless communication and portable computers integrated into clothing [49]. They make a distinction between clothing which is worn to carry out a specific profession (smart uniforms) and clothing which anyone could wear, even in their leisure time (smart clothing).



Multi-purpose uniform

- ✓ Climate protection (PCM and smart gel)
- ✓ Conducting fibres (heat dissipation)
- ✓ Camouflage protection from visible, near IR, IR and radar
- ✓ Provision for radio set, battery pack, and cell phone
- ✓ Wearable computer, sensors and actuators
- ✓ Ballistic protection

**Figure 7.14** A modern soldier with smart clothing and electronic gadgets

Intelligent clothing facilitates person-to-person communication or can accomplish establishment of efficient networking with computers or other access control systems to acquire and transmit global information remotely. All these demonstrate novel routes of working with emphasis upon further simplifying the existing applications and opening up of new fields of applications [50].

## **7.9 High-tech Applications of Smart and Intelligent Textiles**

### **7.9.1 Development of Smart Shirts**

In 1996, the US Navy wanted to develop individual protective equipment for soldiers that could alert the mobile hospitals stationed near a battlefield if a soldier was wounded or shot. Information is instantly passed by the unit to the battlefield coordinator by a personal status monitor developed by US Defense Advanced Project Research Agency. Therefore, using this methodology, the key performance requirements functions (e.g., penetration of a projectile to the soldier's body and vital body signs) can be recognised. Of course, no compromises should be made with the general requirements of the uniform (e.g., wearability in combat operations, durability, maintainability, connectability). 'Wearability' implies that the system should be lightweight, breathable, comfortable (form-fitting), easy to wear and take off, and to provide easy access to wounds. 'Durability' is designed to withstand repeated flexural and abrasion, which are characteristics of combat conditions.

Current smart garments achieve their abilities from conductive organic polymeric fibres being seamlessly integrated into the structure of textiles. This was a major breakthrough in textile engineering because, for the first time, a fully fashioned garment was woven on a weaving machine from a two-dimensional (2D) fabric. The process also results in tightly integrated electronic circuitry being placed into the fabric, which is quite resilient, durable and washable. Specific conductive designs or patterns can be knitted or woven into the textiles with standard processing machinery. Textiles produced by this process can act as sensors for temperature, strain, pressure, humidity, barriers to electromagnetic radiation, anti-static applications and for heating and cooling. Garments and other products manufactured from these textiles could make daily life easier, healthier, safer and more comfortable.

The structure and design processes of the garment should be modular to integrate intelligence but simultaneously be comfortable just as in a typical shirt. The important characteristics are: holding a sensor to detect penetration of a projectile; an electrical sensor to act as a data bus to carry forward the information; and a static dissipating component to minimise static build-up on the garment. These modules can be put together in any desired combination to cater for specific end-use requirements (e.g., for a smart shirt in healthcare applications). Integration of the modules is done during production through selection of appropriate fibres and yarns that provide the specific functionality associated with the building blocks. T-connectors in clothing (similar to button clips) are attached to the yarns that serve as the data bus to carry out the information from the sensors (e.g., electrocardiograph). By making the sensors detachable from the garment, the versatile nature of the garment can be significantly enhanced. The materials described next are chosen as the 'building blocks' of a smart shirt based on their properties and performance requirements:

- Polypropylene fibre/fabric as the base component.
- Plastic optical fibres for the penetration sensing component.
- A copper core with a polyethylene sheath and doped Nylon fibres with inorganic materials for the electrical-conducting component.
- Spandex for form fitting.
- Nega-Stat® (W. Bernet & Son LLC, Arcadia, SC, USA) for the static dissipating component.

### **7.9.2 Snowmobile Garments**

A snowmobile is a vehicle used in remote areas and harsh conditions, such as the Arctic winter. Experienced snowmobile drivers who know how to move around in

an Arctic environment and who have basic first-aid skills face several emergencies. If lost, they must be able to locate themselves and to reach shelter. They must have access to local weather forecasts, knowledge of time for sunrise and sunset and, if submerged in water or if they fall into ice, must be able to get out of water/ice and survive in sub-zero temperatures long enough to be rescued. If their snowmobile breaks down, they must be able to walk in deep snow. If they have an accident and fall unconscious, the suit should send out an automatic distress signal, together with enough information regarding body condition for the rescue units. Furthermore, the suit should provide shelter and make life comfortable in an arctic climate. The objective is to build as many features as possible into the prototype.

Electronic and other devices should be part of the garment rather than inserted; all wires and other devices must be hidden inside and the suit must be comfortable to wear. The maximum weight for the suit should be 4.5 kg; all the devices must work at  $-20^{\circ}\text{C}$  for 24 hours and should be operational even if the wearer falls into water. User interfaces must be designed for use without removing gloves if the fingers are numb from cold, as well as being washable in a conventional washing machine.

A snowmobile suit is usually a two-piece garment consisting of high waistline trousers and a jacket with a hood comprising breathable (but watertight) material as well as special shock-absorbing padding at the knee, elbow and shoulder areas. For comfort and safety, the suit should maintain thermal equilibrium by using PCM. Several sensors are used for monitoring the body functions and movements of the user.

Sensors monitoring heart rate are attached close to the skin and sewn permanently into the underwear. The rest of the sensors are attached to the suit for measuring the external temperature and body temperature. The temperature differences are used for determining the user's position. By measuring the acceleration forces, it is possible to determine if the user has collided with something, whether he/she is moving, or the position he/she is in. Electronic devices are attached to the suit, including the processor and communication network which interfaces in different parts of the garment for connecting different components, interfaces for recharging the batteries, and other consumer options based on necessity. Also, the user interface, interface for power recharging, and wiring are washable, resistant to shock, flexible and abrasion-resistant. Sensors monitoring the heart rate are also in place.

The global positioning system installed into the central processing unit uses several orbiting satellites for radio navigation, providing the user with the ability to locate his/her exact position and to very accurately determine the latitude, longitude, and altitude. The user can also locate the shelter and military unit. A compass with a 'GO TO' arrow is included, with direction and distance to the desired destination also displayed. The power supply is organised from solar panels. To utilise static electricity,

conventional batteries are selected. The smallest battery to guarantee power for 24 hours weighs 600–700 g. The battery is rechargeable at home or from the snowmobile during the drive. The electronics in the suit are usable with both hands without the need to remove gloves. At the back of the garment there is an airtight sack, and by getting into the sack the user can prevent hypothermia for as long as 4 hours. One of the thigh pockets is detachable and fireproof, and can be used for melting snow over a fire. In such situations, to avoid hypothermia, it is important to drink liquids. Waterproof matches, collapsible snow shoes, and a first-aid kit are also provided.

In an emergency, the wearer of the suit can send a distress signal by squeezing the user interface for 30 seconds. The rescue team can confirm the signal back to him/her and also read his/her coordinates. Through various sensors, the suit monitors the condition of the user (e.g., heart rate, g-forces, temperature, pain, hypothermia). If a critical situation is diagnosed by the software, a distress signal is sent automatically. The interface, however, warns the user first and he/she has 30 seconds to cancel the signal if necessary. In addition to just the signal and coordinates, the rescue team will be able to see if the person is moving around, which position he/she is in, whether he/she is in the water, body temperature, and external temperature.

### **7.9.3 Intelligent Textiles in Healthcare**

Health monitoring textile clothing and devices can be used in day-to-day life as comfortable clothing, biomedical and cosmetic care, glucose sensors, smart brassieres, and respiratory syndrome detection of vital signals [51-54]. The human body functions as an automated thermoregulatory system and generates CO<sub>2</sub> and H<sub>2</sub>O in the process of metabolism and muscle activity. The body regulates its temperature by circulating heat by dilatation or constriction of blood vessels, muscle movement and sweat gland activity. A balance between the rates of heat generated by metabolism and its loss to the environment from the body through clothing must be maintained. If thermal resistance offered by clothing is insufficient or the environment is hostile (e.g., if a person stays in sub-zero temperatures for a long time), the body temperature drops.

Far infrared (FIR) is a part of the sunlight spectrum and its wavelength ranges from 4 to 1000 μm. Recent biotechnology studies revealed that FIR has biogenetic effects. FIR can activate, revitalise, reactivate, develop and strengthen various organs in the body if it is absorbed. In the various organs of human body, the circulatory system plays an important part, especially in the microcirculatory system. FIR vibrates at a frequency similar to that of the human body and can penetrate the body, where it activates cells and reactivates as well as strengthens the microcirculatory systems.

Bio-ceramics are the ultimate materials used to store FIR. Three materials are the



most effective: (i) chromic oxide with finely divided porcelain, (ii) chromic oxide with stainless steel, and (iii) ceramic fibres. The effectiveness of chromic oxide with stainless steel, however, is found to fade over time. Certain alloys of nickel have been introduced as radiation generators. Such alloys absorb and radiate all wavelengths or frequencies of light. Of these, only FIR is selectively absorbed by chromic oxide and porcelain, the rest is reflected away. Bio-ceramic-based textiles are part of intelligent textiles. In conventional heat insulation materials (e.g., cotton, hemp, silk, wool, polyester, polyamide, polyacrylic), fibres provide a certain degree of resistance to heat loss, which is determined by the number of air pockets present in the fabric. Solar ray selective clothing absorbs near body temperature. FIR textiles can absorb the body's irradiated FIR radiation and convert it to heat, enhancing thermal resistance and lowering the inner temperature of the clothing. All of these new functional textiles are one-way, thermoregulated heat-insulating materials. To keep the skin temperature within 30.4 °C to 36.4 °C, one must put on or take off this clothing according to the external temperature. If clothing could automatically change its thermal resistance according to the temperature, the inner temperature would not only increase body comfort, but also reduce fatalities.

#### **7.9.4 Implantable Devices**

##### **7.9.4.1 Smart Degradable Sutures**

A newly designed material that is biodegradable is a multi-block copolymer in which block-building segments are linked together in linear chains. Specifically, the polymer created contains a hard segment and a 'switching segment, both with different thermal properties. A temporary shape is created in the form of an elongated fibre, which is then used to loosely tie a suture to close a wound. After increasing the temperature, the suture material shrinks, creating a knot with just the right amount of tension on the surrounding tissue. The polymers used for constructing the sutures are not only smart but degradable in the human body upon long-term exposure. In general, it is difficult to create such a knot in the confined spaces associated with endoscopic surgery. If a knot is fixed with a force that is too strong, necrosis of the surrounding tissue can occur. If the force is too weak, the formation of scar tissue which has poorer mechanical properties is observed, and may lead to the formation of hernias. SMP appear to be one solution to the problem [55].



#### **7.9.4.2 Textile Scaffolds**

Textile structures are an important class of porous scaffolds used in tissue engineering [56]. The basic concept of tissue engineering is to regenerate or to grow tissues or organs by culturing isolated cells from the tissue or organ of interest on porous biodegradable scaffolds as templates. The scaffold acts as an extracellular matrix for the adhesion and growth and/or regeneration of cells. The cells transplanted onto scaffolds multiply and produce tissue matrices that can take up and secrete protein, generate force and resistance, constrain permeability, and exhibit other life processes. A significant amount of research has been carried out to design various types of scaffolds for tissue engineering: foams/sponges, 3D printed substrates/templates, and textile structures. However, there is no universal scaffold that meets all the requirements of various tissues because the optimum tissue engineering conditions vary from tissue to tissue. The flexibility and stiffness of the scaffold should be of the same order of magnitude as surrounding tissues to prevent the scaffold from breaking or collapsing and from stress building from adjacent tissues. In addition to mechanical properties, the optimum design of a scaffold for a specific tissue application requires consideration of microstructural, chemical and biological aspects. Microstructural aspects of textile scaffolds include pore size, porosity, pore size distribution, pore connectivity and reproducibility of pores. These aspects are vital because they provide the optimal spatial and nutritional conditions for cells and determine successful integration of natural tissue and the scaffold.

Among the various materials used for scaffolds, woven fabrics are normally rigid and inflexible due to the tight interlacing of yarns. The next stiff and strong scaffold is the braid. Knits (non-woven) and foams display the lower end of mechanical properties. Of all the scaffolds, knits display considerable deformability and good compliance owing to their looped yarn arrangement. Polymeric scaffold materials used in tissue engineering can be natural or synthetic. Collagen, chitin and starch are examples of natural materials isolated from human, animal or plant tissues which result in high costs and large batch-to-batch variations. In addition, these materials exhibit a very limited range of properties and are difficult to process. Synthetic biodegradable polymers such as polyesters and polyanhydrides can be processed into various shapes and microstructures, and the desired surface area, porosity, and pore size distribution can be tailored for degradation time ranging from days up to several years. Their surface properties can be altered to adapt to the biological requirement for the adhesion, growth and function of cells. It is evident that biodegradable polyester-based materials dominate tissue-engineering applications and are used successfully in various implant applications approved by the US Food and Drug Administration (FDA).

### **7.9.5 Embroidery Technique for Smart Textiles**

Embroidery technology is the art of working on ornamental designs on cloth and leather with decorative stitches. Using this technique, threads can be arranged almost in any direction, which is important for technical/smart textiles, for example, clinical dressings, which are generally in 2D structures but which can be constructed in 3D structures for more critical wounds. On a textile flat substrate, any desirable and dimensionally stable form can be produced by allowing the threads to be arranged in any direction with small motifs and rounded patterns. Unlike in knitted fabrics, the embroidery threads can be placed on top of one another to create a 3D structure. Embroidery machines enable stitching from one material component to another, which generates colour combinations suited to the type of fabric. The combination of embroidery technology and intelligent textiles is similar, and much potential lies in the unconventional use of embroidery [57]. ‘Combined embroidery’ means, apart from the basics of material and embroidery, other additional materials and techniques may be used. These products are categorised as ‘embroidery’ even though other techniques (e.g., padding, shearing) are involved. Technical applications of embroidery include (i) tailored fibre placement (TFP), (ii) stamps and (iii) medical textiles.

In the TFP method, the embroidery is done to create fibre-reinforced composites to withstand complex forces through fibre orientation. A cord of reinforcing fibres (glass, carbon, aramid, hybrid yarns) is sewn onto the ground material. Woven or non-woven fabrics can be used as the ground material on which the cord is to be embroidered. In this process, the ground materials become part of the composite and coordinate with the matrix material. Embroidery for stamp technology, by virtue of the small size of the textile structures and self-adhesive coatings, has made its use possible. However, although this technology has great promise, its use as a standard practice to produce stamps is expensive. Medical textiles are another important area of use of embroidery technology where the products range from simple gauze or bandage materials to scaffolds for tissue culturing and various prostheses for permanent body implants.

### **7.9.6 Bio-processing of Smart Textiles**

With the increasingly important requirement for textile manufactures to reduce pollution in textile production, the use of enzymes in the chemical processing of fibres and textiles is rapidly gaining wider recognition because of their non-toxic and eco-friendly characteristics. Enzymes are biological catalysts. All enzymes are made of protein, which is why they are sensitive to heat, pH and heavy metal ions. Unlike ordinary catalysts, they are specific to one chemical reaction. A conventional catalyst may be used for several chemical reactions, but an enzyme works only for one specific reaction. Enzymes must have the correct shape to do their job. Their

activities are dependent upon several factors (e.g., duration of reaction, variation of pH during the course of the reaction, ionisation of its active sites) and at high temperatures the activity is considerably reduced. Enzymes are absorbed on the surface of a substrate and accelerate hydrolysis of the substrate at its active sites. Intermediate products of decomposition of the substrate are formed and the enzyme is released to be absorbed again on different locations on the substrate. Finally, the substrate molecule is converted into end product and the enzyme is regenerated. Conventional chemical processes are generally severe, and fibre damage may occur. However, enzymes are characterised by their ability to operate under mild conditions. Hence, enzymic processes may take place without harm to the fibre. Enzymes are also readily biodegradable and therefore potentially harmless and environmentally friendly.

#### ***7.9.6.1 Usage of Enzymes in Textile Processing***

In the manufacture of textiles, several chemicals are used at the different stages of processing (e.g., desizing, scouring, softening of cotton, denim washing, silk degumming, wool scouring) and may cause environmental pollution. Therefore, textile processing industries are trying to use environmentally friendly chemicals and processing techniques. One of the intrinsic properties of wool is its shrinkage, which modifies the fibre surface. In such cases, a protein disulfide isomer is used as a shrink-proofing material that rearranges the disulfide bonds. This introduces additional crosslinks in the substrate, leading to improvement in the shrinkage resistance without impairing the texture of the material. The whiteness and lustre of wool can also be enhanced by bleaching the fibres with  $\text{H}_2\text{O}_2$  and dithionite or bisulfate in presence of protease. Treatment of wool prior to dyeing with an enzyme improves dye uptake and improves colour-fastness.

The use of enzymes in cotton finishing has been found to be more popular than with wool. The composite structure of the bulk of this fibre restricts enzyme treatment to the surface, which leads to the desired effects of lustre and softness in cotton finishing. The enzyme used for complete desizing of cotton is diastase. Bio-polishing or defuzzing of the cotton fabric upgrades the quality of the fabric by removing the protruding fibres from the surface to make it soft, and the method is called 'singeing'. In bio-polishing, the enzymes also prevent pill formation, and generate increased smoothness of the product. The effect of enzymic treatment on the colour yield of cotton in dyeing is negligible.

Untreated jute is not affected by enzymes, whereas the scouring of jute with alkali makes it susceptible. If the scoured fabric is first treated by enzymes followed by bleaching, the whiteness index is more than that produced by only scouring and direct bleaching. If the enzyme treatment is carried out after bleaching, the whiteness

index of the fabric is decreased due to back-staining. Enhancement of the bleaching effect due to enzyme treatment saves up to 25% of  $H_2O_2$ . Increase in pore volume and peroxide retention capacity due to enzyme treatment results in enhancement of the bleaching effect. Efforts are being made to evolve new enzymes to meet the vast potential in smart fibres. Types of some enzymes for cellulosic textiles are given in Table 7.4.

Table 7.4 Types of enzymes for cellulosic textiles	
Enzyme type	Action on cellulose
Amylase	To decompose starches during desizing
Catalases	To act on hydrogen peroxide and decompose it into oxygen
Proteases, lipases, pectinases	A suitable combination of all the three work as scouring waxes and natural colouring matter
Laccases	Work as a decomposing agent for indigo dyes
Cellulases	Wash down the surface effect on protruding cellulosic fibre polishing of denim and other materials

## 7.10 Role of Nanotechnology In Textiles

‘Nanomaterials’ (materials with at least one dimension ranging between 1 nm and 100 nm) are basically of three types:

- Nanolayers which have only one dimension in the nano range (e.g., layered clay/silicate);
- Nanofibres, which have two dimensions in the nano range (alumina, boron carbide, silicon carbide, carbon); and
- Nanoparticles, which have all the three dimensions in the nano range (spherical carbon black, fullerene, magnetic nanoparticles, silicon dust).

Nanomaterials are likely to have an enormous impact and to completely change the way textiles are processed or the products that will be manufactured. Nanotechnology can be used to create new or improved textiles and structures through molecular engineering for controlling the design at the molecular scale. They can be used to create unique properties in everyday fabrics and modify the finishing or coating characteristics applied to conventional fibres or fabrics. The scope of incorporation of nanotechnology into textiles does not compromise the basic properties (i.e., breathability, launderability, durability) of the base fabric but makes them multi-functional. Nano-processed garments can be self-repellent to water, oil and beverages or protective against chemical toxicants or gases. If finished with additives of sizes <100 nm, the processed clothing becomes structurally more compressed and becomes stain- and dirt-resistant or protective against viral or bacterial attack. Use of nanomaterials as additives to coated textiles can also generate very good permeability to water vapour, which allows good ventilation, reduces moisture absorption, and increases comfort and crease-resistant features. Nano-processed textiles and clothing are non-toxic (thus addressing environmental concerns), remain bright, are fresh looking, and are more durable than conventional garments, but remain cost-effective. Other significant achievements of the introduction of nanotechnology in coated textiles are:

- The mechanical properties of the fibres, e.g., tensile strength, modulus and tear resistance can be significantly improved.
- Production of fibres, textiles and clothing can be envisaged via desktop manufacturing, allowing customised textile forms, colours, and designs.
- Functional capabilities, e.g., flame resistance and barrier properties of textile fabrics and finished garments will be readily achieved.

### **7.10.1 Carbon Nanofibres**

Carbon nanofibres have a length of 5–100  $\mu\text{m}$  and a diameter of 5–100 nm. Although polyacrylonitrile (PAN) and its copolymers have long been used routinely in the textile industry, it was only recently that they have been produced in fine scale fibres by the electrospinning technique [58-60]. Unlike conventional fibre spinning techniques, which can produce polymer fibres with diameters down to the micrometer range, electrospinning can produce polymer fibres with diameters in the nanometer scale. In electrospinning, electrostatic forces are used to drive the fibre spinning process. The resulting nanofibres exhibit unusually high porosity and surface area. The electrospun PAN fibres can be carbonised in a vacuum at high temperatures. The degree of crystallinity and morphology of the deposited fibres are found to be dependent upon the chemical nature of the catalyst, composition of the reactant gases, and temperature. Liu and co-workers reported on the electrospinning of

poly meta-phenylene isophthalamide nanofibres with diameters <10 nm with good thermal stability that were subsequently coated with carbon, copper and aluminium using plasma-enhanced chemical vapour deposition and physical vapour deposition methods [61]. The conductivity of a single fibre shows that the residual carbon and hydrogen content decreases with pyrolysis temperature and time. There is a strong relationship between the conductivity, carbon and hydrogen content and graphite mole fraction. A new type of fibrous carbon material has been developed from the metal catalysed decomposition of certain hydrocarbons at temperatures of 400-800 °C [62, 63]. The nanofibres thus obtained exhibit high surface area (300-700 m<sup>2</sup>/g), which in turn constitutes sites for chemical or physical interaction namely adsorption. The use of sub-micron fibres with low density, high porosity, and high surface area have attracted the attention of technologists and industries for applications related to filter media, development of separation membranes, wound dressings, artificial organs, protective clothing for bioactive filters for viruses, anti-static fabrics and as well for military use. Recent research has also demonstrated that nanofibres can be produced from polymers using conjugate spinning techniques and designing special spinnerets with productivity similar to other melt-spun fibres. The results have produced fibres in the range 100–400 nm.

### **7.10.2 Clothing-grade Fabrics**

Nanotechnology has been found to be promising for clothing applications [64, 65]. A very small amount of carbon nanotube, carbon nanofibre or metallic nanofibre/particle (alumina, boron carbide, silica, silicon carbide) can be incorporated during the processing of clothing-grade fibres (PP, PE, polyethylene terephthalate, Nylon) which is sufficient to bring about a significant improvement in the breaking strength of the fabrics. Incorporation of nanoclay, modified with quaternary ammonium salt, into PP fibres can create dye sites favourable for lower cost dyeing of clothes. Nanoclays incorporated into textiles have improved stain- and water-resistance without sacrificing the surface feel. The current focus is on the development of an ultra hydrophobic material with excellent water repellency and self-cleaning ability without possessing traditional heaviness and stiffness, utilising the so-called 'Lotus approach' (i.e., creation of surface roughness of textiles in the nano-scale through adoption of innovative surface modification techniques) [66]. Incorporation of nanoparticles such as nanoclays and carbon nanofibres with variable shapes, size, topography/roughness and suitable technology is feasible to improve the attachment of nanoparticles by grafting different polymers with low surface energy onto the substrate fibre/fabric surface, but these are critical factors. The technique has also been found to be beneficial for improvement of the thermal and flammability properties of textiles. Electrophoretic deposition of silicon and boron carbides, silica and carbon whiskers impart better thermal insulation properties for fire-retardant clothes.

A novel approach of Burlington Industries is that of using coating of carbon ‘nano-whiskers’ that are 1/1000 the size of an individual cotton fibre applied to cotton fabric to induce water repellency (Nano-Care®). The changes in the fabric are quite undetectable and do not affect the natural touch, softness and breathability of the fabric. These whiskers cause the water to roll-off the fabric, and semi-solids (e.g., ketchup, salad dressing) can be readily lifted off and the fabric made stain-free by regular washing or laundering. Nano-Dry® is a hydrophilic finishing technology applicable to polyester or Nylon garments for sportswear and underwear that require perspiration absorbency with minimum alteration of colour. The technology is ~50 times more effective than home laundering. The same company has come up with Nano-Touch finishing technology, which gives a durable cellulosic wrapping over a synthetic fibre core. The product is superior to synthetic fibres in terms of hydrophilicity, anti-static properties and lustre but simultaneously possesses strength and durability similar to that of any synthetic fibre. Several commercial products using membranes of PTFE derivatives have been developed that present an analogy with the Lotus effect.

### **7.10.3 Speciality Fabrics**

Intelligent textiles for personal protection and safety especially in a NBC environment are extremely important [67, 68]. Seamless garments are useful in impenetrable protection suits in which the seams are created by deposition of electrospun nanofibres and can be used with enhanced safety, comfort and breathability. Woven fabrics are unsuitable for such applications. In space, the fabric used for spacesuits needs to protect the wearer from widely varying and extreme environmental conditions. Nano-encapsulation is a viable way of meeting such requirements. Incorporation of nanoclay or surface deposition of nanofibres or nanowhiskers on fabrics improves barrier properties which are highly essential for applications such as fabrics for parachutes, hot-air balloons and inflatables. Nanocomposites of multiwalled carbon nanotubes (CNT) in polymers are used in lightweight personnel flexible armour. An overview of protective clothing, their applications, materials requirements and market potential has been given by Smith [69].

Pressure suits (‘g-suits’) are used by pilots when flying fighter planes. Current g-suits designed using hydraulics and pneumatics show slow response and often limit manoeuvres that the pilot can safely carry out. Blood can instantly pool into the abdomen and extremities and cause the pilot to pass out. One possible solution is to develop a specialised suit that squeezes the lower body, forcing blood to flow back through the torso and up towards the head. Researchers have developed materials for ‘artificial muscle’ to perfect a pressure suit which can also be suitable for other therapeutic or commercial devices. Non-woven electrospun nanofibres in the form of



fabrics made from piezoelectric copolymer have been used for the wings of exceedingly small (20 g) micro-air reconnaissance vehicles and as felts being tried out in filtration due to their extremely high specific surface area, absorbency and retention capacity. Artificial muscle fibres in g-suits can be woven into a suit to apply variable restrictive and counterpoint pressure to the body. The suits may be skintight, light, and designed to change to handle any situation to provide greater strength. Another important application for this technology would be to integrate smart artificial muscles with helmets. If a person's head is hit with a bullet or in a plane crash, wearing a helmet may not be sufficient to save life. A hard hit against the helmet transfers to the skull, causing concussion or death. Smart artificial muscle fibres can react on impact, stabilising the head and transferring or distributing the forces to the shoulders and the rest of the body.

E-textiles are another promising application of nanotechnology [54]. These materials can be used for fabrication of sensitive detection systems for faint signals in battlefields. Nanowire-incorporated fabrics are examples of such materials. Smart detection systems for chemical and biological warfare agents, dispersed in air or water, can be realised by 'smart dust-incorporated fabrics'. Using a laser torch, the presence of these toxic agents trapped on the textile surface can be detected.

#### **7.10.4 Nanotechnology in Biomedical Applications**

Nanodispersed hydrogels and encapsulated CNT incorporated into fabrics are used for controlled drug release over a predetermined time period. Polymeric scaffolds of nanofibres are finding interesting applications for tissue engineering, preferential destruction of cells, and wound healing due to their very high surface area and better biocompatibility. Polypyrrole nanofibres are used extensively as biosensors for artificial nerve regeneration and artificial heart muscles.

Donovan Industries launched 'Dawn Mist Bleach-Wipe', a disposable towel that can prevent blood-borne contaminations (e.g., tuberculosis, HIV, hepatitis B), thereby protecting medical workers at hospitals against infections [70]. Tiburon is a microfibre composite containing three fabric layers: an absorbent fluid-control layer, an impermeable membrane, and a patient-comfort layer. The top layer holds and disperses fluid, keeping it from pooling on top of the patient and leading to contamination.

### **7.11 Summary of Applications of Smart and Intelligent Textiles**

Microencapsulation of PCM has already become a successful technology for



commercial applications in pharmaceutical and agrochemical industries. However, the technology has immense potential in the textile industry, especially in functional coatings for obtaining functional surfaces. This area has remained largely unexplored. The technology also allows for the combination of properties of different materials that are difficult to envisage with other available technologies. The high cost of microencapsulation is prohibitive, but can be justified by the added value of the products. The worldwide demand for functional coatings is likely to increase, so new, cost-effective microencapsulation technologies are bound to evolve and will remain in the forefront of research. At present, the major focus from scientific and industrial communities is towards development of methods to provide functional coatings on fabric surfaces that are easy to apply and have long-term stability. Use of micro-encapsulated paraffin wax is such an application. It is directed towards making climate-controlled dresses for civil and military applications taking into account the advantages of paraffins for their heat release or storage properties in the vicinity of human body temperature. As the phase change occurs with the outside environment, increase in the heat transfer area with volume change of the storage material inside MPCM shell polymeric materials is variable according to need. Also, the scope of their repeated use to withstand frequent changes in environmental temperatures is another advantage.

Use of SMP with the possibility for triggering the shape memory effect in the vicinity of normal body temperature is advantageous for the development of clothing items. Metallic shape memory alloys are usually incorporated in the shape of a spring placed between the layers of a garment, the gap between the layers can be substantially increased above the activation temperature and reversibly becomes flat below the activation temperature. This characteristic improves protection of the human body against external heat. In place of a metallic shape memory alloy, SMPU films can be incorporated between the adjacent layers of clothing. If the temperature of the outer layer drops sufficiently, the polyurethane film develops an out-of-plane deformation. This results in broadening of the air gap between the clothing layers, giving sufficient insulation to the wearer to keep him/her comfortable in harsh climatic conditions. The deformation, however, must be strong enough to resist the weight of the clothing, sustain flexibility required for the movements of the wearer, and must be reversible in effect if the outer layer of the clothing is exposed to warmer conditions.

The main challenges of achieving smart textile materials are to evolve an effective surface-modifying system based on a biocompatible polymer and establishment of surface adhesion of textile fibres for a durable coating by the introduction of new chemical groups to the substrate surface. Chitosan-based hydrogels on textiles are in an initial development stage.

The main application of conductive smart textiles is in the development of garments which offer electromagnetic interference (EMI) shielding. Conductive fibres braided into a shield or sock offer superior EMI performance, they are anti-static and also increase thermal conductivity in clothing for sports wear. Another application of these garments is in antennae to receive electromagnetic waves and for the power supply of electronic devices in garments. Smart fibres containing graphite particles can conduct electricity where the resistance of the fibre is changed with the change in temperature. As the material warms, it expands and reduces the conductivity between graphite particles to regulate the passage of electricity and keeps the temperature stable. The current generation of smart garments are obtained by seamlessly knitting or weaving individual conductive fibres with specific conductive designs or patterns into the textiles with standard processing systems and machinery. These garments get their properties from conductive polymers being tightly integrated into the fabric to make it resilient, durable and stable, but the functionality of the system may be fragile. Textiles produced by the new process have the potential to act as sensors for temperature, strain, pressure, humidity, and chemicals.

Considerable progress needs to be made for coating textiles by dielectric elastomers before achieving commercial viability for direct applications. A multidisciplinary approach requires development of fibre-like actuators and sensors in fabrics and textile structures to achieve effective integration. The large simulated displacement achieved so far is encouraging, and this approach should remain a mainstream research area in terms of applications and designs.

Thermochromic textiles obtained through the application of thermochromic dyes undergo colour change at specific temperatures. However, these fabrics are considered to be only fashionable materials. To establish application of these fibres for sophisticated, thermal sensors, stealth and camouflage applications, it is necessary to improve upon their temperature endurance and to establish accurate sensing and colour changing abilities.

Photochromic organic polymers used as coating or finishes to textiles or incorporated into textiles by bi-component or electrospinning processes can show reversible changes of colour or conductivity with the influence of electromagnetic radiation. The molecular arrangement of polymeric materials can alter the absorption and reflectance spectra of the organic molecules under different monochromatic electromagnetic radiations, and lead to alteration of the colour of incident and reflected radiations. The areas of application include fashion design and construction of solar UV protective garments.

The organic photoluminescents (photoluminescent or electroluminescent types) are rigid compounds (molecular or polymeric) which possess good molecular conjugation and a relaxation mode that allows the emission of a photon. Photoluminescence and

optoluminescence of optical fibres is used for the manufacture of textiles that emit light for screens. Electroluminescent phenomena of smart textiles are similar to those of flexible organic light-emitting diodes, and have been utilised for the manufacture of flexible screens for wearable computers. Other applications include electroluminescent yarn for fashion garments as well as for high-visibility protection equipment.

Another way to profit from smart materials in the textile industry is to use their intrinsic properties as sensors in electronic devices, application of solar cells for charging batteries/cellphones/walkie-talkies and in e-textiles. A new field of investigation is the deposition of photovoltaic devices on textile substrates.

The textile industry has the biggest customer base in the world. Therefore, advances in customer-oriented products should be the focus for future nanotechnology applications. The discovery of CNT has led to the development of high strength and superior performance fibres by electrospinning processes which can significantly enhance the strength and conductivity of the fabric after suitable heat treatment. Hence, these nanofibres and yarns can also be efficiently used as supercapacitors in electronic textile compounds. It has also been shown that by simultaneous reduction of fibre diameter and increase in twist (1000 times), nanoyarns can be spun, like multiwalled carbon nanotubes, to generate specific mechanical properties such as strength, toughness and energy-damping capability. These characteristics can then be deployed to produce electronic textiles for supporting multi-functionalities such as capabilities for actuation, energy storage, radio or microwave absorption, electrostatic discharge protection, textile heating, or wiring for electronic devices. The recent advancement of fabric finishes is used for cotton fabrics which provide desirable properties (e.g., absorbency, breathability, softness) but have limitations due to their inferior strength, durability, crease resistance, dirt resistance, and flame resistance. Conversely, synthetic fibres are very strong, crease-resistant and dirt-resistant, but lack comfort properties. With recent advances in nanotechnology, it is possible to develop next generation, cotton-based fabrics with complementary advantages of cotton and manmade fibres by blending both of them or by treating the yarns or fabrics with various design/material modifications at the nanoscale [71]. Chemical deposition technology is advantageous for surface polymerisation (graft copolymerisation) of polymer fibres and textiles with the deposition of conducting electroactive polymers resulting in composite materials with high tensile strength, good thermal stability and increased electrical conductivity for effective application in microwave attenuation, EMI shielding, and dissipation of static electric charge. They are useful for military applications (e.g., camouflage, stealth technology).

It is hoped that the scope of development of smart polymers and growth of nanotechnology will significantly contribute in the opening up of new possibilities for the development, design and manufacturing of smart and intelligent clothing in

co-operation with other sectors of science and engineering. With this strategy, it may also be possible to exploit the largest commercial potential of development of more efficient and attractive products combined with the minimum risk of investment and marketability. Experts anticipate smart clothing and use of nanotechnology in textile applications to appear on the market within the next 5–10 years.

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# 8 Some Methodologies for Testing and Quality Control of Domestic and High Tech Polymer Coated Textiles and Fabrics

**A.K. Sen**

## **8.1 Introduction**

Coated textiles have applications in defence, transportation, healthcare, architecture, space, sports, environmental protection, and many other diverse uses. Coated fabrics have an important place among technical textiles. Testing of the coated fabrics is of great importance. There are several tests to evaluate coated textiles. This chapter gives an overview of the test methods typical to coated fabrics, explaining the basic principles and relevance of the tests. Tests that are common to uncoated textiles such as dimensions, tensile strength, and tear resistance have not been included. ASTM D751 [1] is a compilation of the test methods for coated textiles. It specifies that the time lapse between curing of the fabric and testing should be >16 hours. Specimens are cut in such a way so that no specimen is nearer to the product edge than one tenth of the width of the fabric. Before carrying out the test, the specimens are conditioned at specified temperature and humidity depending on the standard being followed [ASTM, British Standards (BS), Indian Standards (IS)]. Besides the general tests for coated fabrics listed in ASTM D751, there are special tests for fabrics for a specific end use, for example, cyclic ageing for airbag fabric, light transmittance for architectural textiles, air retention for fabric for rafts, and oil resistance for fabrics used as fuel containers. These tests have also been included in this chapter.

Protective clothing for chemical warfare agents is usually constructed from coated fabrics. These fabrics are of two types: impermeable and permeable. Impermeable suits are made from elastomer-coated fabric that does not transmit water vapour. Permeable suits are water vapour permeable and are usually active carbon coated fabrics. Evaluation of the protection capability of these fabrics is also described.

## **8.2 Coating Mass per Unit Area (BS 3424 [2], IS 7016 Part 1 [3])**

The principle of the test method is to remove the coating from the textile substrate

by a stripping solution. The stripping solution depends on the type of polymer used for coating. Circular, rectangular or square specimens of 2,500 mm<sup>2</sup> area are taken from the roll and weighed. The result is expressed in mass per unit area (g/m<sup>2</sup>). The bulk of the coating is removed from the fabric with the aid of stripping solution/solvent. The remaining coating is removed by Soxhlet extraction using a stripping solvent, washed with acetone, dried and weighed. The Soxhlet extraction is repeated until a constant weight of the specimen is obtained. The coating mass per unit area (g/m<sup>2</sup>) is obtained from the difference between the weight of the original specimen and that of the stripped specimen. The stripping solvent for polyvinyl chloride (PVC) is tetrahydrofuran or methyl ethyl ketone. For natural rubber on cotton, nitrobenzene or xylene is used. Polyurethane (PU) is stripped by a 2 N solution of potassium hydroxide (KOH) in alcohol.

In a rubberised fabric, the rubber content can be determined directly or indirectly. In the direct method, natural rubber is estimated from the acetic acid generated by oxidation of the coating by chromic acid. Similarly, determination of chlorine and nitrogen content permits estimation of Neoprene or nitrile rubber in the coating (IS 5915 [4] and IS 6110 [5]). In the indirect procedure (applicable to olefinic rubbers) non-rubber ingredients such as filler, accelerator, and sulfur are determined from acetone, chloroform and alcoholic KOH extracts. The rubber content is obtained from the difference.

### **8.3 Bursting Strength and Puncture Resistance (ASTM D751 [1] and IS 7016 Part 6 [6])**

Two standard methods are described. Method A uses a tensile testing machine with a ring clamp. For method B, a diaphragm bursting tester is used. Method A is used if risk of mechanical damage to the material is more relevant, whereas a hydraulic bursting method is useful for fabrics if pressure resistance is important.

**Method A** uses a tensile testing machine with a bursting attachment. The specimen is held securely between two ring clamps with an internal diameter of 45 mm at the centre. A polished steel ball of 25 mm diameter is positioned at the centre of the test piece. The size of the specimen should be  $\geq 12.5$  mm greater than the outside diameter of the ring clamp. During testing, the steel ball moves vertically towards the specimen at 300 mm/min until the test piece ruptures due to the pressure of the steel ball. The force caused to rupture the test specimen is noted.

**Method B:** The specimen is held between two circular clamps of 75 mm diameter having a circular aperture of 30 mm diameter. An elastic diaphragm exerts pressure

on the fabric specimen by introduction of water at a constant rate. The pressure required to rupture the specimen is noted.

Puncture resistance is similar to method A except that the steel ball is replaced by a piercing instrument shaped like a flared flat tip screw driver having a width of 8 mm and a thickness of 0.8 mm at the extreme tip. The force required to completely penetrate the specimen is noted.

#### **8.4 Hydrostatic Resistance (ASTM D751 [1], BS 3424 [2], IS 7016 Part 7 [7])**

Hydrostatic resistance or resistance to water penetration is of great importance for evaluating the functional properties of coated fabrics used in rainwear, covers and inflatables. ASTM describes two procedures: one uses a Mullen-type hydrostatic tester, and the other uses hydrostatic pressure of a rising column of water.

In the Mullen-type apparatus, a specimen of coated fabric is secured between two circular clamps of 75 mm diameter with a co-axial aperture of 31.2 mm. An O-ring is placed in the lower clamp for making a watertight seal. Hydraulic pressure is generated by forcing water by a piston into the device. A Bourdon gauge measures the pressure generated. Hydrostatic pressure is applied to the underside of the clamped specimen such that the coated side is exposed to water pressure. Pressure is increased steadily until water appears on the other side of the specimen. This pressure is noted. Alternatively, 14 kPa pressure is applied for 5 minutes. If there is no permeation of water, the sample is considered as having passed the test. This method is not applicable for fabrics having water resistance <25 kPa.

In the water head method, a 200 mm<sup>2</sup> specimen is placed on a clamp of 170 mm external diameter and 115 mm internal diameter provided with a rubber gasket. A water chamber in the shape of a dome is placed on the upper plate. The water chamber has a water inlet, and a vent. A water leveler consisting of a water inlet, a water outlet and an overflow pipe is attached to the inlet of the water chamber. The overflow pipe provides a means of maintaining a constant level of water. The head of water is increased by raising the water leveler by a motorised system at 1 cm/s. The pressure at which a first drop of water appears at the underside of the specimen is noted. Alternately, a head of water is kept steady for a specified period and leakage (if any) noted.

### **8.5 Cone Test (IS 7941 [8])**

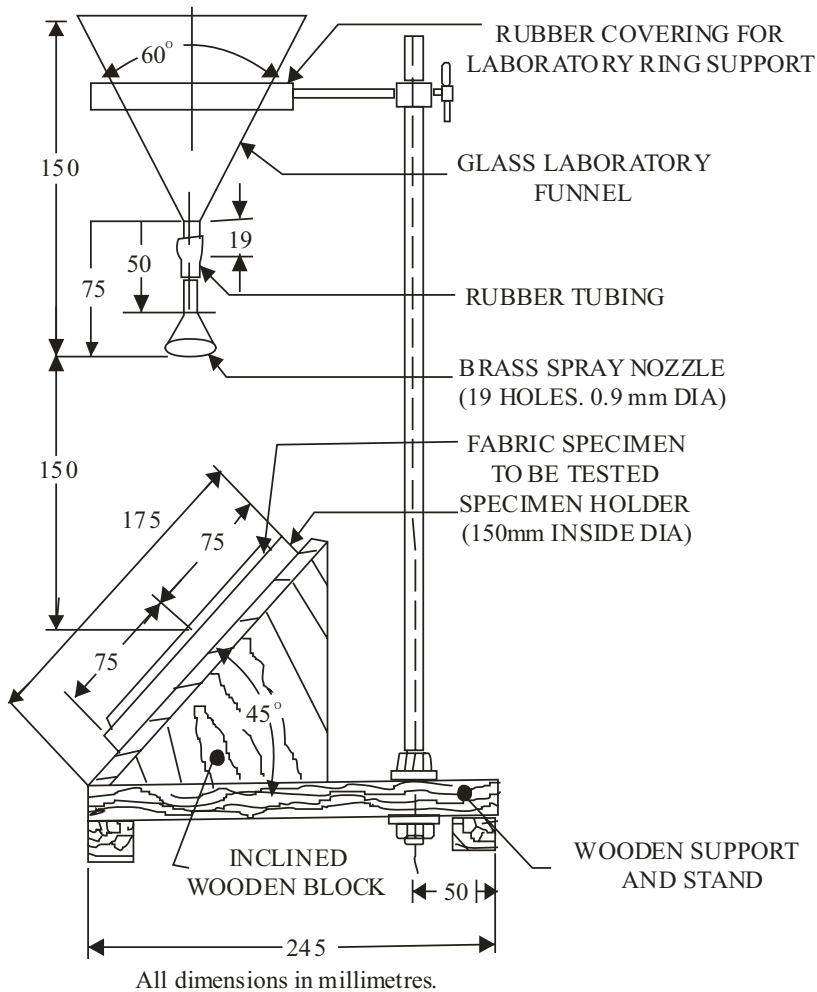
This test evaluates the water-proofness of the fabric where it is locally stressed. A circular or rectangular specimen is folded twice and then opened to form a cone. The fabric folds sharply at the tip of the cone and is heavily stressed. The cone of the specimen is then placed in a wire cone which in turn is placed in a glass funnel and filled with specified amount of water. The whole assembly is in a graduated cylinder. After a specified period (18 hours), penetration of water and wetting of the outer surface of the specimen is noted.

### **8.6 Water Repellency – Spray Rating Test (IS 390 [9], AATCC 22 – 1996 [10])**

For various end-use applications the uncoated side of the fabric is given a repellent treatment. This test assesses the repellency of the fabric to water. The apparatus used for the purpose is shown in **Figure 8.1**. It consists of a 250 ml glass funnel to the stem of which is attached a metal spray nozzle (to spray water) and is fitted on a metal stand. The specimen has the dimensions 18 × 18 cm and is fixed in a circular metal hoop of 15 cm diameter so that the fabric is taut. The hoop containing the sample is placed on a wooden block 15 cm below the nozzle and at 45° from the horizontal. The glass funnel is filled with 250 ml distilled water and sprayed on the fabric for 30 seconds. The specimen is then taken out and tapped gently. The wetted area is compared with standard photographs to obtain the spray rating.

### **8.7 Adhesion of the Coating to the Fabric (ASTM D751 [1])**

This test is important because if the adhesion is inadequate the coating may separate from the fabric substrate. The test is conducted in an autographic strength testing machine. A set of three specimens of dimension 25 × 200 mm are cut in a longitudinal direction and cross-direction. If the coating is thick (i.e., the strength of the coating is more than the adhesive bond between the coating and the fabric), the coating is peeled from the fabric by a diagonal cut with a knife starting 50 mm from the top of the specimen. The coating is separated ≤50 mm from the starting point of the cut. The separated plies of the specimen are clamped to the upper and lower jaws of the testing machine. The rate of traverse specified in ASTM is 0.85 ± 0.05 mm/s or 5.00 ± 0.02 mm/s. Peeling is done for a minimum of 76 mm. The adhesive strength is determined from the load required to separate the coating layer. The mean test value of at least three specimens in longitudinal and cross direction are reported as force in N/25 mm.



**Figure 8.1** Apparatus for the spray rating test taken from IS 390. Reproduced with permission from the Bureau of Indian Standards (BIS), New Delhi, India [9]

If the coating is thin, two specimens are bonded face-to-face by a suitable adhesive, leaving 50 mm free. For PVC coated fabric the adhesive may be a solution of PVC in tetrahydrofuran and for a PU-coated fabric a suitable PU adhesive is used. Specimens are cut from the adhesive line of the bonded specimen up to 50 mm so that one ply is the base fabric and the other ply contains both layers of coating and the base fabric. The two parts are clamped into the jaws of testing machine and adhesive strength determined as described previously. ASTM tests and IS 7916 Part 5 [11] are similar.

Adhesive strength can also be determined by a dead weight apparatus (BS 3424 [2]). The apparatus consists of two grips: the top grip is fixed rigid to a support and the bottom is free. The separated plies of specimen are fixed in two grips. Weights in units of 200 g are placed in the lower jaw until separation occurs. This load is recorded.

### **8.8 Low Temperature Bending Test (ASTM D2136 [12], IS 7016 Part 10 [13])**

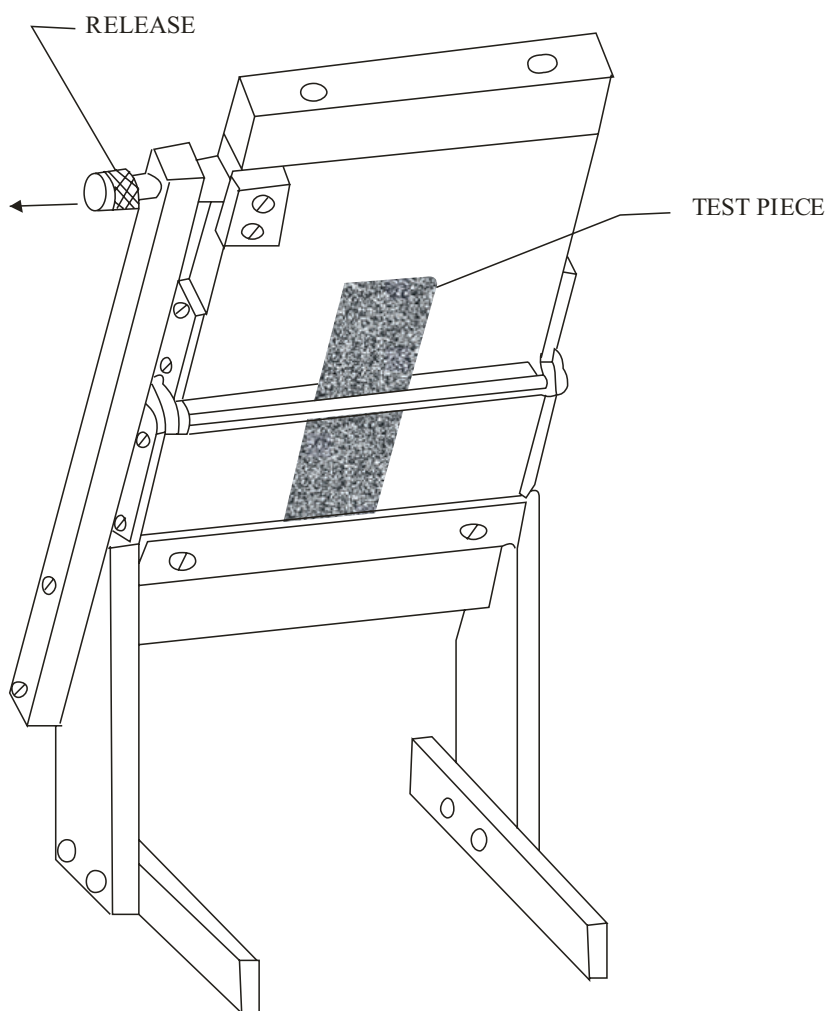
In many applications, coated fabrics undergo low temperature flexing. The low temperature bending test is used to evaluate the suitability of coated fabrics for low temperature application. For carrying out the test, specimens sized 25 × 100 mm are cut. The test specimens are placed in-between glass plates to prevent curling and kept in a low temperature chamber for four hours for conditioning. A bending jig (Figure 8.2) is also placed in the low temperature chamber. The jig consists of two rectangular aluminium blocks mounted on a frame joined by a hinge and aligned in a straight line at 60° from the horizontal. A weight of 250 g is attached to the upper block. A release mechanism folds the hinge to 180°. After exposure of the specimen, it is placed in the jig and bent within the chamber with the aid of a release mechanism. Specimens are examined for cracks and fractures under ×5 magnification.

### **8.9 Brittleness Point of Flexible Polymers and Coated Fabrics (ASTM D2137 [14], BS 3424 [2], IS 7016 Part 14 [15])**

This ASTM method covers the determination of the lowest temperature at which rubber vulcanisates and rubber-coated fabrics show brittleness due to crack formation. Method B of the specification is for coated fabrics. In this test, specimens are given impact at low temperature. The lowest temperature at which cracks appear is known as the ‘brittleness temperature’.

Specimens sized 40 × 6 mm are die-punched in such a manner that the longer dimension is parallel to the lengthwise direction of the coated fabric (Figure 8.3). The specimens are conditioned at 23 ± 2 °C at 50 ± 5% relative humidity (RH); ASTM D751 [1]. A minimum length of 6 mm of the fabric is held firmly by a clamp, forming a cantilever. A striker is positioned over the specimen. The striking edge has a radius of 1.6 mm. The clearance between the striking arm and the clamp varies with the fabric thickness (note 2 of the ASTM specification/IS 7016: Table 1). For example, for a thickness of 1.65 mm to 2.20 mm, the clearance is 6.4 ± 0.3 mm. The striking edge impacts the fabric by solenoid activation at 2 m/s. The test procedure consists of exposing the entire test assembly to low temperature in a low temperature liquid bath of methanol

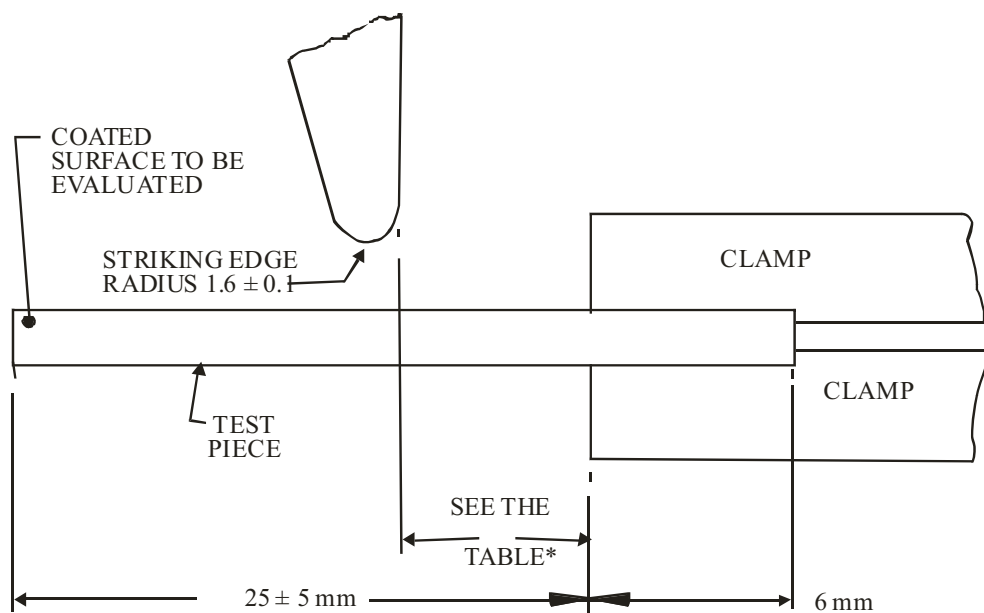
or silicone in a refrigerated cabinet. After temperature equilibration, impact is applied on the specimen by the striker, and cracks in the coating examined by folding it at  $180^\circ$  at  $\times 5$  magnification. The temperature of the bath is lowered in steps of  $10^\circ\text{C}$  until the specimen fails. The temperature of the bath is then raised by intervals of  $1^\circ\text{C}$  until the specimen passes the test. A temperature  $1^\circ\text{C}$  below this point is the 'cold crack temperature' or brittleness temperature.



**Figure 8.2** Low temperature bending jig taken from IS 7016 part 10. Reproduced with permission from the Bureau of Indian Standards, New Delhi, India [13]



In the BS method, a folded test piece of specimen is placed on an anvil in a low temperature bath. The brittleness temperature is obtained using the previously mentioned procedure.



**Figure 8.3** Low temperature brittleness tester taken from IS 7016 Part 14. (\* refers to Table 1 in IS 7016 Part 14). Reproduced with permission from the Bureau of Indian Standards, New Delhi, India [15]

### **8.10 Accelerated Ageing Test (BS 3424 [2], IS 7016 Part 8 [16], ASTM D751 [1])**

Different types of ageing tests are described in the specifications depending on the end-use requirement and type of fabric. They are heat ageing, oxygen pressure ageing, ozone ageing for elastomer fabrics, weathering for architectural fabrics, cyclic ageing for airbag fabrics and loss of plasticiser for PVC-coated fabrics.

Determination of heat ageing is described in ASTM D751 [1]. This test is for comparative evaluation and does not correlate with deterioration due to weathering.

In this test, the physical properties of the specimens from the roll are determined at the outset. Common physical properties are visual inspection, breaking strength, bursting strength and tear strength. Specimens are then placed in an air oven at a specified temperature and for a specified time. The BS and IS suggest a temperature range of 70-100 °C and duration of 168 hours. After heat ageing, the physical properties are again measured and deviation from the original expressed as a percentage.

The oxygen pressure ageing test is specified in IS 7016. In this test, specimens are hung in a pressure chamber of stainless steel at an oxygen pressure of 2000 kN/m<sup>2</sup> and 70 °C for 24 hours, and deviation of physical properties from the original reported.

ASTM D1149 [17] describes an ozone cracking test for elastomer-coated fabrics. Specimens are placed around a mandrel to impart strain, and placed in an ozone test chamber containing a mixture of air and ozone (50 mPa - partial pressure of ozone) at 40 °C. After a specified period, specimens are examined for cracks using a magnifying glass.

For airbag fabrics of automobiles (which are lifesaving devices), a stringent ageing test has been specified in ASTM D5427 [18]. Test specimens are tested for cyclic ageing at various temperatures and humidity, heat ageing, humidity ageing, and ozone ageing. Cyclic ageing is done in the following sequence of conditions: -40 °C, ambient humidity for 29 hours; 22 °C, 95% RH for 19 hours; 107 °C, ambient RH for 29 hours; and 22 °C, 95% RH for 19 hours. Heat ageing is done at 120 °C for 336 hours and humidity ageing is carried out at 80 °C, 95% RH for 336 hours. For ozone ageing, the conditions are 40 °C, 65% RH, ozone concentration 50 pphm and duration 336 hours.

Architectural textiles that are used outdoors are tested by accelerated weathering. ASTM D4851 [19] specifies three types of weathering test using any of three types of lamps: xenon arc, sunshine carbon arc, and ultraviolet (UV) fluorescent lamp. Each lamp has different spectral characteristics and none correlate with natural weathering. The type of lamp to be used is specified by the user. The physical properties evaluated are tensile and tear strength.

### **8.10.1 Lifetime Estimation by Ageing Studies**

Attempts have been made to study the kinetics of the degradation of elastomers from measurement of the changes in physical properties at elevated temperatures for different periods. Among the various physical properties are tensile strength, modulus, hardness, and elongation at break. The latter showed the largest changes with time of ageing; as such, this was found to be suitable for kinetic studies. From

the kinetic study, the energy of activation of degradation was estimated. With the aid of kinetic data, it is possible to calculate the period of time before a reasonable loss of property occurs: known as the threshold ageing period (TAP). From a knowledge of the TAP at different temperatures, it has been possible to estimate the shelf-life of an elastomer at a particular temperature. Such a method can also be adopted for polymer-coated fabrics.

### **8.11 Test Methods for Determination of Volatile Loss (ASTM D1203 [20])**

The performance specifications of vinyl- and PU-coated upholstery fabrics specify a test for estimation of loss of plasticiser and volatiles from the fabric (ASTM D3690 [21]) by ASTM D1203 [20]. Loss of volatiles and plasticiser is an important parameter because it gives an idea of the durability of the fabric. The procedure involves absorption of volatiles from the specimen by active carbon at elevated temperature and measuring the loss of weight. A metal container of ~100 mm diameter and 500 ml capacity is taken. Activated carbon (120 ml) of specified mesh size is placed at the bottom of the container. A weighed test specimen of 50 mm diameter disc is placed over the carbon layer, followed by another layer of active carbon. The three specimens are placed in the container containing an active carbon layer on top of the third specimen. The active carbon layer is thus at the top and the bottom and in-between the specimens. The closed container is placed in an oven at 70 °C for 24 hours. Specimens are weighed after the test and the weight loss noted.

In an alternate method, specimens are placed in the annular space of a cylindrical metal cage of bronze gauze and are not in direct contact with active carbon. This method is considered to be more accurate. The wire cage method is also specified in BS 3424 [2]. In the IS method (IS 1259 [22]), specimens are exposed at 100 °C for 24 hours in an air oven and the volatiles estimated by weight loss.

### **8.12 Blocking Test (ASTM D751 [1], IS 7016 Part 9 [23])**

‘Blocking’ of coated fabrics means that two fabric surfaces, when kept in contact, separate with difficulty and damage the coating. This test is to check the tackiness of the coating at elevated temperature so that the coating of the fabrics is not damaged if stored in rolls. The procedure adopted in both specifications is similar.

In the ASTM test, specimens sized 200 × 200 mm are cut. Specimens are folded face-to-face, then back-to-back, making a square of 100 × 100 mm. The square is placed between two glass plates with a weight of 1.8 kg on the top of the plates. The

assembly is kept in an oven at 70 °C for 6 hours. At the end of the exposure period, the assembly is taken out, cooled, and specimens examined for adhesion between layers or damage to the coating. The test is done for at least three specimens.

In the IS method, six specimens sized 150 × 150 mm are cut. Specimens are arranged in three pairs: face-to-face, face-to-back and back-to-back. The three pairs are placed one over the other so that a pile of 100 mm<sup>2</sup> is formed, leaving the rest of the area free. The pile is placed between two glass plates. A 5 kg weight is placed on the top glass plate and the assembly exposed in an oven at 70 °C for 3 hours. After the test period, specimens are examined for adhesion or damage to the coating. This method examines the blocking between coated and uncoated surfaces.

In the BS method, two specimens sized 150 × 75 mm are cut. Specimens are placed one over the other face-to-face. A load of 1.5 kg is placed on half the area of the specimen pair. The assembly is exposed to 60 °C for 15 minutes. After exposure, the assembly is cooled, and a 100 g weight attached to the lower free end of the specimen. No blocking is reported if the upper strip separates freely from the lower strip.

### **8.13 Wicking Test (ASTM D751 [1])**

Specimens sized 2.5 × 8 cm are cut from warp and weft directions. A beaker is filled with water and dye solution up to a depth of 5 cm. The colour of the dye should be contrasting in colour to the base fabric and coating. One end of the specimen is dipped 2.5 cm in water in a lengthwise direction for 24 hours at 21 °C and 50% RH. After the test, the coating of the specimen is cut above the immersion line at regular intervals of length. The length up to which staining of the base fabric has occurred is noted. The wicking length is reproduced to the nearest millimetre.

### **8.14 Degree of Fusion (or Degree of Curing) of the Coating (BS 3424 [2], ASTM D4005 [24])**

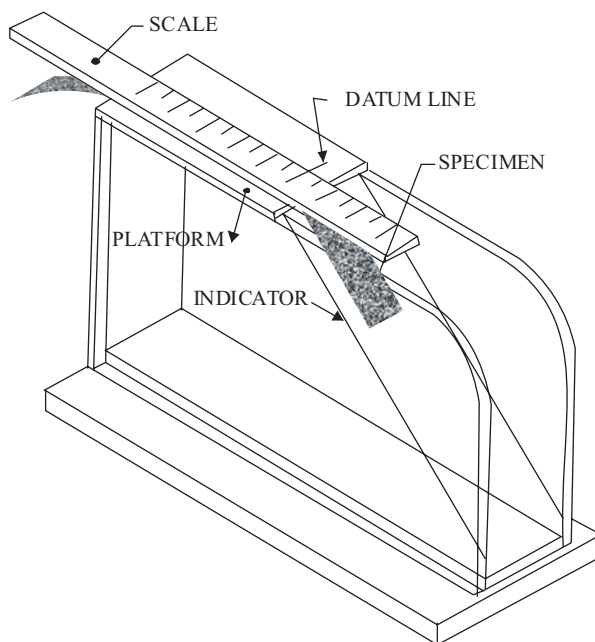
PVC coating is done by dispersion of PVC in a plasticiser. Upon heating, phase inversion occurs, resulting in a fused homogeneous mass on the fabric. Appropriate fusion is essential for the durability of the coating. This test determines appropriate fusion of the PVC film.

In the ASTM test procedure, three test specimens sized 20 × 40 mm are cut and wrapped around glass rods with the coated side outward. They are then dipped in a beaker containing acetone for 15 minutes at 23 °C. Samples are then examined for cracking or disintegration of the coating. The BS procedure is similar except that it

is carried out at 20 °C. For rubber fabrics, specimens are immersed in xylol at 27 °C for 2 hours and examined for tackiness. The sample is considered to be cured if no softening, tackiness or detachment of the coating is noted.

### 8.15 Stiffness of Fabric Test (IS 6490 [25])

This standard describes a method of determination of stiffness of textile materials. A coating on a textile makes the fabric stiffer, and this method measures the extent of stiffness. The principle is to measure a particular length of fabric specimen which, when set up as a cantilever, bends to a constant angle by its own weight. For this purpose, a stiffness tester is used, which consists of a smooth metallic platform of 40 × 200 mm size mounted on a frame and is kept horizontal by a spirit level. Below the platform is an indicator at 41.5° below the plane of the platform (**Figure 8.4**). A scale 25 × 200 mm weighing  $10 \pm 2$  g graduated in millimetres with a rough bottom is used for pushing the specimen.

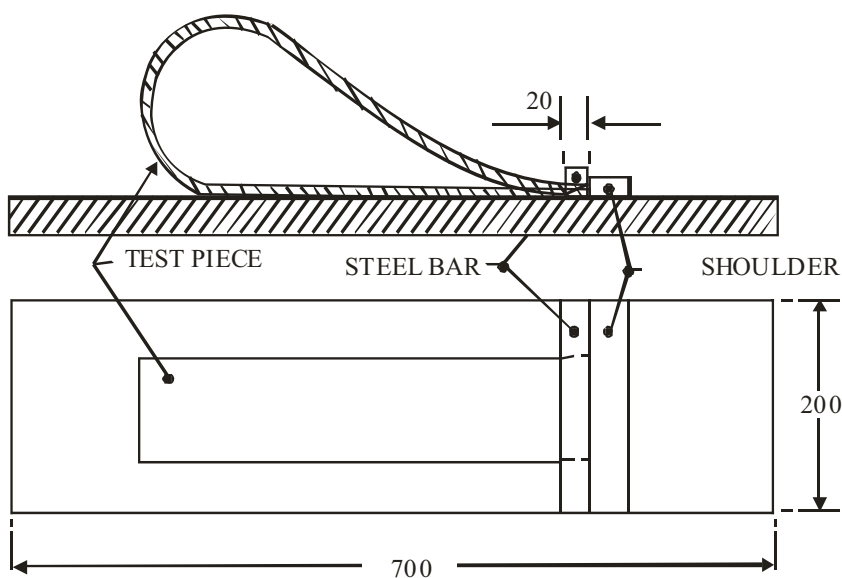


**Figure 8.4** Stiffness tester taken from IS 6490. Reproduced with permission from the Bureau of Indian Standards, New Delhi, India [25]

Test specimens  $25 \times 200$  mm in size are cut from warp and weft directions. A specimen is placed lengthwise on the platform and the scale placed over the specimen. The edge of the specimen and zero of the scale coincide with the datum line drawn on the platform. With the aid of the scale, the sample is pushed forward steadily beyond the edge of the platform. An increasing part of the specimen will overhang and start bending under its own weight. When the edge of the specimen coincides with the inclined line drawn on the indicator, the length of the overhang is noted from the scale. This is the 'bending length' of the fabric. The higher the bending length, the lower is the stiffness of the fabric.

### 8.16 Flexibility Flat Loop Method (IS 7016 Part 11 [26])

This is a simple test for determining the flexibility of a polymer-coated fabric. Specimens of  $600 \times 100$  mm size are cut from warp and weft directions. A loop is made of each specimen held by a steel bar and is placed on a horizontal plane (Figure 8.5). The height of the loop is measured, which gives an idea of the flexibility of the fabric. The lower the height of the loop, the greater is the flexibility.

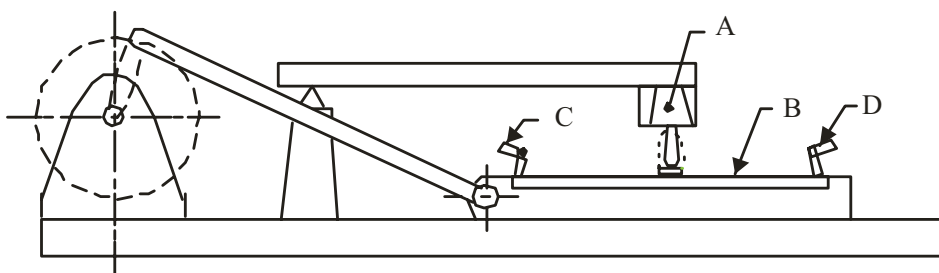


**Figure 8.5.** Flat loop tester for flexibility taken from IS 7016 Part 11. Reproduced with permission from the Bureau of Indian Standards, New Delhi, India [26]

### **8.17 Colour Fastness to Dry and Wet Rubbing (BS 3424 [2], IS 1259 [27])**

This test evaluates durability of the colour on the coated fabric. The procedure consists of rubbing the coated side of the fabric by white muslin under a specified load and number of cycles. Stains (if any) imparted on the muslin are noted. The test is done by a crockmeter (**Figure 8.6**). The apparatus consists of a glass plate upon which a specimen of  $230 \times 50$  mm size is placed and secured firmly by grips. An abrader peg 16 mm in diameter is fixed to a pivot by an arm. The abrader peg imparts a reciprocating motion in a straight line parallel to the surface of the specimen.

In the test procedure, a specimen is mounted on the glass plate. A piece of white muslin 25 mm in diameter is wrapped around the abrader. The abrader is then set in motion. The specified stroke length of the abrader is 100 mm, rate of traverse 15 cycles/min, and the load on the specimen 0.5 kgf. In dry rubbing, the muslin is examined for stain after 10 abrading cycles and compared with a greyscale standard. In wet rubbing, muslin is wetted with soap solution prior to rubbing.



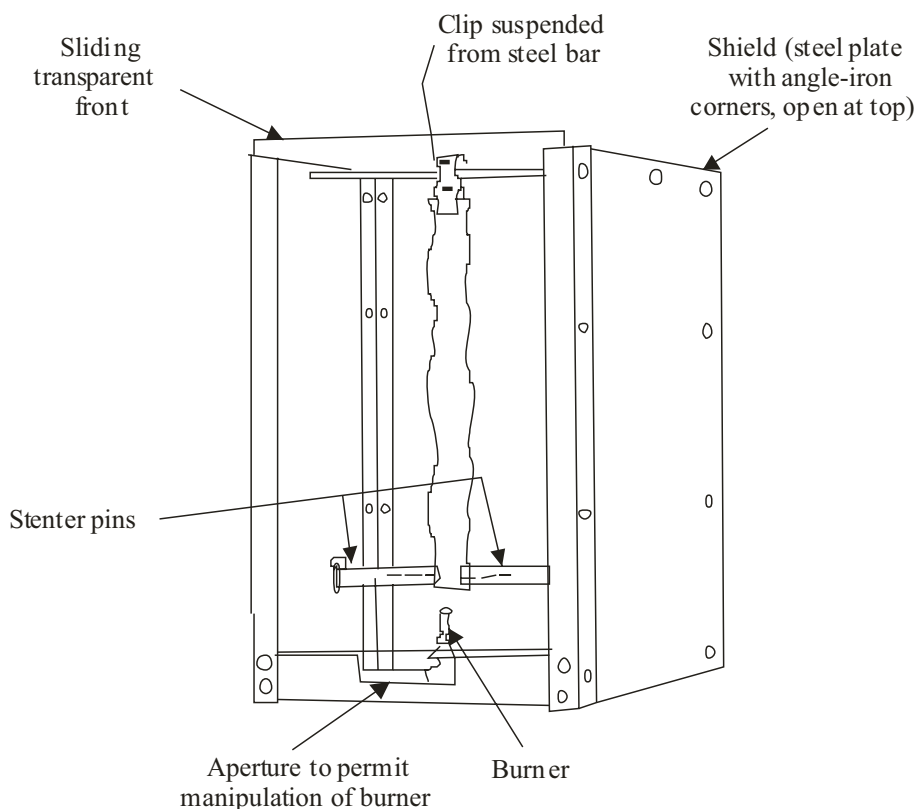
**Figure 8.6** Crockmeter taken from IS 1259. A) Abrader; B) glass plate; C) and D) grips. Reproduced with permission from Bureau of Indian Standards, New Delhi, India [27]

### **8.18 Flame Resistance Test (IS 11871 [28], BS 3119 [29])**

Flame resistance is an important property of coated fabrics used for upholstery, furnishing, and protective clothing. There are various tests for measuring the flammability of fabrics, but the vertical flame test described in the previous standards

is widely used. Basically, the test measures the flame propagation, after glow, and char length of a fabric specimen when held vertically over a specified flame for a specified time.

The apparatus consists of a non-combustible box sized  $305 \times 305 \times 250$  mm with a sliding transparent front (Figure 8.7). An aperture 25 mm deep and 125 mm long is provided at the bottom of the front door to allow handling of the gas burner. Test specimens ( $315 \times 50$  mm) are cut in the warp and weft directions. A specimen is hung from the rod in the box by a clip. The lower end of the specimen is held taut by a stenter pin and ignited by a butane burner. A flame is applied at a specified distance from the lower edge of the specimen for 12 seconds. The flame is then removed, and the time of flame propagation after glow and char length is measured.



**Figure 8.7** Vertical flame tester taken from IS 11871. Reproduced with permission from the Bureau of Indian Standards, New Delhi, India [28]



### **8.19 Abrasion Resistance Test (ASTM D3389 [30], BS 3424 [2])**

This test method covers the resistance of coated fabrics to abrasion. In all the tests of this type, the coated fabric is abraded by an abrader, and the loss of mass provides information on the abrasion resistance of the fabric.

In the ASTM specification the apparatus used is known as a 'rotary platform double-headed abrader'. Circular test specimens of 110 mm diameter are cut and placed with the coating side up on a circular platform which is rotated by a motor at 70 rpm. Two abrasive wheels attached to the free end of two pivoted arms are mounted on the specimen. The abrasive wheels rest on the specimen so that a vertical force is applied on the specimen by them. The apparatus is provided with weights for varying the vertical force of the abrader wheels on the specimen. Abrasion occurs due to friction between the rotating specimen and the abrasive wheels. Vacuum cleaner or compressed air is used for removing the abraded particles. The result is reported as mass loss after a specified number of rotations or number of rotations required until the end point, i.e., when all the coating is removed.

The BS specifies that a Martindale tester should be used for expanded vinyl fabrics. The machine consists of a rectangular base plate upon which are attached four silicon carbide paper discs of specified grade. A top plate contains four specimen holders to which are attached four circular specimens. The top plate rests on the lower plate in such a manner that the coated side of the specimens in the sample holder rests on the centre of the abrading discs. A specified load can be applied on the specimen by placing weights thereon. Abrasion occurs due to rotation of the top plate with specimens against the abrading surface of the bottom plate. The pattern of rotation changes from circle to ellipse and then again expanding from ellipse to circle. The number of cycles required for exposing the cellular structure of the fabric is noted.

### **8.20. Method for Determination of Air Retention (ASTM D5193 [31])**

This test is used for evaluating rubberised fabrics used for making pneumatic articles such as floats, buoys, pontoons, weather balloons and rafts. These articles must retain air to carry out their function.

The test apparatus consists of a sample holder that comprises a hollow circular metallic container with a circular orifice of  $330 \pm 3$  mm size on the top to hold the sample. Two ports are provided in the container: one for air inlet and the other for pressure gauge. Bolts are provided at the periphery of the container. For testing, specimens of  $330 \pm 3$  mm are cut from the fabric rolls and holes punched at the periphery

conforming to the size and location of the bolts of the sample holder. The specimen is then mounted on the sample holder by aligning the holes in the sample with the bolts in the container so that the side of the fabric which will be contact with air is face-down. A rubber gasket is placed on top of the specimen. A flange with a collar is placed on the specimen and clamped by nuts and bolts.

A layer of (1–2 mm) soap solution is poured on the exposed surface of fabric and air pressure of 20 kPa applied for 10 minutes. The fabric passes the test if air bubbles do not appear. This test is limited to coated fabrics having a thickness <3 mm.

### **8.21 Damage Due to Flexing Test (ASTM D2097 [32], BS 3424 [2], IS 7016 Part 4 [33])**

The ASTM specification is meant for measuring the flexibility and adhesion of upholstery fabric used for shoe uppers. The synthetic leather is mechanically flexed alternately from a flat position into a single or a double bend. At the end of the specified number of cycles, the leather is examined visually for cracks and separation of coating. The apparatus used for the test is a Newark flexing machine. The instrument consists of two pistons: one is stationary and the other movable. The movable piston traverses at 500 rpm with a stroke of 32 mm. In the closed position, two pistons are kept apart at a distance of 15 times the thickness of the specimen. Test specimens of 76 × 114 mm size are cut and their ends clamped to the two pistons. After the required number of cycles of flexing, the specimen is examined for evidence of peeling and cracks.

IS and the BS standards specify that the De-Mattia test apparatus should be used. The apparatus consists of a pair of flat grips which traverse in a vertical plane. The traverse distance is 57 mm between the open and closed positions and the rate of traverse is 300 cycles per minute. Specimens of 45 × 125 mm are cut from the roll in longitudinal and cross directions. Each test specimen is folded 15 mm from each of the longer sides to a width of 15 mm. The folded specimens are clamped between the grips of the apparatus and flexed for a specified number of cycles (~100,000). After flexing, the specimens are examined for peeling and cracks.

### **8.22 Hydrolytic Stability of Upholstery Fabric (ASTM D3690 [21])**

This test covers the determination of changes in the physical properties of coated fabrics due to elevated temperature and high humidity. The physical properties determined are tensile strength, abrasion, flexing, and adhesion. A large sample of the fabric is exposed to 70 °C and 95% RH in an humidity chamber for 15 days. After exposure, the sample is conditioned for 24 hours at 21 °C and 68% RH. Specimens

from the sample piece are cut and tested for the physical parameters mentioned above, and compared with those of the original. The percentage loss of the property is then estimated.

### **8.23 Air Permeability Test (BS 3424 [2])**

Coated fabrics are normally impervious to air, but waterproof breathable fabrics that have a porous discontinuous coating are permeable. The pores impart breathability or water vapour permeability. Air permeability is expressed as volume of air in millilitres that passes through per  $\text{cm}^2$  of the fabric per second at a pressure head of 100 Pa. The apparatus used is based on the Shirley Institute UK air permeability tester.

The specimen is clamped between two circular flanges having a circular orifice of 25 mm diameter. A vacuum pump sucks air through the specimen. The flow of air across the specimen is regulated by a series valve and a bypass valve so that the pressure drop across the specimen is 1 cm water head. After the steady state of pressure head is reached, the rate of flow is measured by a rotameter.

### **8.24 Water Vapour Permeability Test (ASTM E96 [34])**

This test is essentially required for waterproof breathable fabrics because compact coated fabrics are normally impervious to water vapour. The ASTM method is not only intended for textiles but also other materials, including paper, plastic, and wood. Two methods are described in the standard: the desiccant method and the water method. The former measures gain in weight of desiccant and the latter loss in weight of water due to transport of water vapour.

*Desiccant method* - In a shallow dish having a mouth with an area of 3,000  $\text{mm}^2$  with a ledge is placed a layer of >12 mm of anhydrous calcium chloride of specified mesh size. The test specimen is placed on the ledge of the mouth of the dish, and the edges sealed with molten wax. There should be a gap of 6 mm between the desiccant layer and the specimen. The entire assembly is placed in a chamber whose temperature and humidity can be controlled. The temperature is normally maintained at 32 °C and 50-95% RH depending on the environment desired. The weight gain of the test assembly is measured periodically. A plot of weight gain against elapsed time is drawn. From the slope of the straight-line plot, and area of the test specimen exposed, water vapour permeability is obtained as  $\text{g/h/m}^2$ .

*Water method* - In this method, the dish is filled with distilled water to a depth of 3-5 mm, leaving a gap of ~20 mm from the specimen. The rest of the procedure is

same as of the desiccant method. The weight loss is measured periodically and water vapour permeability calculated as described as for the desiccant method.

BS 7209 [35] meant for waterproof breathable fabrics and is based on the water method. In this method, specimens are tested along with a reference fabric. The latter is made of high tenacity monofilament yarn of 32  $\mu\text{m}$  diameter having an open area of 12.5%.

The procedure consists of placing specimens and reference fabric on shallow dishes containing distilled water. The fabric and specimens are sealed over the mouth of the dish. The gap between the underside of the specimen and the surface of the water is kept as  $10 \pm 1$  mm. and the specimens are kept taut. All the dishes are placed on a rotating turntable in a chamber in which the humidity and temperature is maintained at 20 °C and 65% RH. The turntable is rotated slowly to avoid formation of still air; care is taken that the gap between the specimen and water surface is not altered. After one hour, the dishes are weighed to permit equilibration of water vapour. The dishes are placed back on the turntable in the chamber and weighed after 16 hours. The permeability of water vapour is given by  $24 M/At$ , where  $M$  is the loss of mass in g,  $A$  the area of the fabric in  $\text{m}^2$ , and  $t$  is time in hours. The result is expressed as  $\text{g}/\text{m}^2/24$  hours. The water vapour permeability index ( $I$ ) is the ratio of water vapour permeability of the specimen and reference fabric.

### **8.25 Resistance to Permeation by Hazardous Liquid Chemicals (ASTM F739 [36])**

Coated fabrics are widely used for protective clothes used against chemical spills. This test describes a method for measuring the permeation of hazardous liquid chemicals through protective clothing. The apparatus consists of a glass cell with two compartments. The test specimen is placed in between these compartments. One compartment is filled with the hazardous chemical and the other with a suitable solvent to collect the permeated material. The test specimen forms a barrier between the challenge chemical and the collecting fluid. The latter may be a liquid or a gas in which the hazardous chemical is fully soluble. The chemical permeating through the specimen dissolves in the collecting fluid and is analysed periodically by common analytical techniques such as UV and infrared spectrophotometry, gas liquid chromatography, and colorimetry. The breakthrough time (BTT) is determined from the time elapsed between initial contact of liquid with the sample until it is detected by the analytical tool. Barrier properties of the specimen are determined from the BTT and permeation rate.

### **8.26 Resistance To Penetration By Blood-borne Pathogens (ASTM F1671 [37])**

Healthcare professionals are vulnerable to infection from the body fluids of patients. This is particularly true for hazardous blood-borne pathogens such as hepatitis B, hepatitis C, and human immunodeficiency virus (HIV). Special clothing is worn by healthcare workers to protect them from these pathogens. This test is useful for evaluating the barrier property of the fabrics used for protective clothes. The test is carried out by a simulant microbe suspended in a simulant body fluid. The test equipment is a penetration cell of ~60 ml capacity which is filled with a bacteriophage (a virus that infects bacteria) and pressurised by air. The fabric specimen of the material for protective apparel acts as a barrier for the challenge suspension of the bacteriophage. Penetration of the suspension at the other side of the fabric is observed visually, and penetration of microbe is tested by a microbiological assay. The microbe for the test is bacteriophage  $\phi$ -X-174 lysate in a nutrient broth. Bacteriophage  $\phi$ -X-174 lysate is a stimulant for hepatitis B and C as well as HIV. The nutrient broth is a stimulant for body fluid. The pressure time sequence for the test is 0 kPa for 5 minutes, 13.8 kPa, for 1 minute, and 0 kPa for 54 minutes. After the test period, the other side of the specimen is examined visually for penetration of liquid. The outer side of the specimen is rinsed with sterile nutrient broth and assayed for test virus by a standard procedure. The specimen is considered to have passed the test if no penetration of liquid and bacteriophage  $\phi$ -X-174 is observed.

### **8.27 Test Method for Coated Fabrics Used for Oil Spill Control and Storage (ASTM F715 [38])**

Coated fabrics are used for the storage of petroleum products such as aviation turbine fuel and diesel fuel, and are used for controlling oil spills in the sea. The test evaluates coated fabrics used for this purpose.

The procedure consists of measuring the physical properties of original specimens. These include mass, thickness, tensile strength, elongation at break, tear strength, adhesion, puncture resistance, abrasion resistance and blocking resistance. The specimens are then immersed in containers filled with diesel fuel grade number 2 (ASTM D975 [39]) for 96 hours. To prevent curling of the specimens, a small weight can be attached to the end of the specimen. The container with the specimen is kept in a chamber at  $23 \pm 2$  °C and  $50 \pm 5$  RH (ASTM D543 [40]). After the exposure period, the specimens are wiped, visually examined for tackiness, swelling, and loss of gloss. All physical properties are tested and compared with those of the original samples. In addition, the low temperature bend test and ozone resistance test are

also done. From comparison of the results of the original and immersed samples, the suitability of the fabric for its end-use application is judged.

### **8.28 Fire Test for Roof Coverings for Architectural Textiles (ASTM D4851 [19] and ASTM E108 [41])**

For the flame test of architectural textiles, ASTM D4851 offers five test options. Each test procedure is distinctly different because the procedure to be applied depends on the purchaser and supplier. In this section, the test procedure of ASTM E108 is discussed. This fire test covers the measurement of the fire characteristics of roof coverings under simulated fire originating outside a building. It forms the basis for relative comparison of roof coverings by measuring the surface spread of flame, and the ability of roof coverings to resist fire penetration from the exterior to the underside of a roof deck under the conditions of exposure. There are three classes of tests: class A - severe; class B - moderate; and class C - light.

The apparatus consists of a test roof deck 1 m wide and 1.3 m long made from pine lumber and mounted on an adjustable frame at a desired incline. The other items of equipment are a gas burner (source of flame), a wind tunnel, air velocity meter, a pressure gauge, a control valve and an adjustable air supply. The shape and size of the flame depends on air turbulence near the apparatus. The temperature of the flame for class A and class B tests is  $760 \pm 28$  °C and for class C is  $704 \pm 28$  °C. All openings of the test room are closed but a free outlet of air is provided by an exhaust. A roof covering is applied on the test deck with a 2.5 cm overhang. An air seal is provided along the sides of the roof covering to restrict air flow under the system during a fire test. Three main tests are conducted: intermittent flame test, spread of flame test, and the burning band test. They are discussed next.

*Intermittent flame exposure test:* A test deck mounted on a frame and covered with a roof covering is subjected to a luminous gas flame with a calibrated air supply to produce the desired air current. For a class A test, 15 cycles of 2 minutes duration of flame and 2 minute flame-off period are applied. For class B, 8 cycles of the same intermittent supply of flame is applied. For class C, 3 cycles of 1 minute flame on and 2 minute flame-off is prescribed. The air supply is maintained after the last application until all evidence of flame, glow and smoke has disappeared.

The appearance of a sustained flame ( $\geq 5$  s) on the underside of the test deck, production of flaming and glowing debris, displacement of portions of the test sample, and falling away of the roof deck is observed.

*Spread of flame:* Adhering to the set-up of intermittent flame test, 10 minutes of flame is continuously applied for class A and class B tests and 4 minutes for a class C test. The distance to which flaming of the material has spread, production of flaming debris, and displacement of portions of the test specimen is observed.

*Burning brand test (burning or charred log):* Test brands are made of rectangular pieces of fir or pine timber into a grid of  $305 \text{ mm} \times 57 \text{ mm}$ ;  $152 \text{ mm} \times 57 \text{ mm}$  and  $38 \text{ mm} \times 19.8 \text{ mm}$  for class A, B, and C types of tests, respectively. The brands are burnt by a flame and the glowing brands placed on the test sample on the test deck. The test is continued until all the brand is consumed. Sustained flaming or glowing debris, and exposure or falling away of portions of the deck is observed.

## **8.29 Noise Reduction Coefficient of Architectural Textiles (ASTM D4851 [19], ASTM C423 [42])**

Architectural textiles are tested for sound absorption by ASTM C423 [42]. This test method covers the sound absorption in a reverberating room by measuring the decay rate and the sound absorption of an object. A reverberating room is designed so that the reverberating sound field closely approximates to a diffuse sound field in the steady state (i.e., when the source is on) and during decay after the sound source is stopped. The sound sources are loudspeakers and sound diffusion is achieved by reflective panels.

A band of random noise is used as a test signal for a period so that the sound pressure level reaches a steady state. When the sound is turned off, the sound pressure level will decrease and the decay rate in each frequency band is obtained from the slope of the straight-line decay curve. The absorption of the room and its contents are calculated from Sabine's formula (Equation 8.1):

$$A = 0.9210 Vd/c \quad (8.1)$$

where  $A$  = sound absorption coefficient in sabines/ $\text{m}^2$ ,  $V$  = volume of the reverberating room in  $\text{m}^3$ ,  $c$  = speed of sound, and  $d$  = decay rate in  $\text{Db/s}$ .

After measuring the sound absorption coefficient of the room, specimen material of specified size is placed in the room. The sound absorption is measured. The sound absorption coefficient of the specimen is obtained from the increase in sound absorption due to the material per unit area of the specimen ( $\text{m}^2$ ).

### **8.30 Solar Optical Properties of Architectural Fabrics (ASTM D4851 [19], ASTM E424 [43])**

The solar optical properties of translucent architectural fabric made from polytetrafluoroethylene-coated glass fabric are determined by solar heat gain or light transmission through the fabric. The data are useful for building designs. In this section, solar energy transmission through the fabric is described as laid down in ASTM E424 for determination of the solar energy transmission of sheet material.

The apparatus is a box capable of supporting 0.61 m<sup>2</sup> specimen. The box can be faced in any direction using a universal mount. The inside of the box is painted black. The sensor element is a pyranometer, which consists of a set of concentric rings of thermopile, coloured alternately black and white. A thermopile is composed of thermocouples usually connected in series that convert thermal energy into electrical energy. The voltage output of the pyranometer is proportional to the total solar radiation. The spectral sensitivity of the pyranometer ranges from 280 nm to 2800 nm, encompassing the entire solar spectrum. The pyranometer is placed in the box 50 mm below the bottom plane of the sample. The pyranometer has a viewing angle of 180°. A recorder measures the output voltage of the pyranometer, which is in the millivolt range. A sample with a size of 0.61 × 0.61 m size is placed on the box on a clear sunny day. The sample is exposed to the sun's rays for ~15 minutes until a steady reading is obtained. The procedure is repeated without a test sample. The solar energy transmission of the specimen is the ratio of the energy measured with the test specimen and without it.

### **8.31 Lifetime Estimation and Biodeterioration Studies by Thermogravimetric Analysis (TGA)**

#### **8.31.1 Life Estimation**

The life expectancy of a polymeric material is important at different stages of its application. These include the retention of desirable properties from the time of manufacturing up to its assembly as well as ageing of the component in the assembled form in equipment located in a strategic position under various environmental conditions.

Estimation of life expectancy is of paramount importance for guaranteed service performance (especially for critical application for products in defence and aerospace) and also for user confidence in other critical applications. Lifetime prediction is done



by the study of kinetics of degradation at elevated temperature by isothermal or non-isothermal methods. However, the former is time consuming. The non-isothermal method (dynamic method) developed by Flynn and Wall [44] is preferred.

TGA is used to monitor weight change in a material as temperature increases. It offers a viable alternative to oven ageing to predict lifetime estimation of a material. In TGA, the material is heated at several heating rates (usually more than three) through its decomposition region. From the resultant thermal curves, the temperature for a constant decomposition level ( $T_c$ ; percentage weight loss, e.g., 5%) is selected. From a plot of the logarithm of the heating rate *versus* the reciprocal of  $T_c$ , a straight line plot is obtained, the slope of which is the activation energy. Toop [45] postulated a relationship between activation energy and the estimated lifetime of polymers using Equation 8.2:

$$\ln t_f = E/RT_f + \ln [ E/\beta R + P(X)_f ] \quad (8.2)$$

where  $t_f$  = estimated life to failure (min),  $T_f$  = failure temperature or selection of operational temperature,  $R$  = gas constant,  $P(X)_f$  = a function whose value depends on  $E$  at the failure temperature, and  $\beta$  = heating rate in  $^{\circ}\text{C}/\text{min}$ .

Gupta and co-workers [46] carried out the lifetime estimation of a flame-retardant bromo-butyl composition of bromobutyl rubber-coated Nylon used in chemical warfare protective suits by Toop's method using high-resolution TGA. It was found that at 25  $^{\circ}\text{C}$  the shelf life was 4.18 years, which dropped sharply to 145 days at 50  $^{\circ}\text{C}$ . Analyses of evolved gases was also done by a mass spectrometer coupled to the TGA. Thermal decomposition of the rubber composition was accompanied by the evolution of  $\text{Br}$ ,  $\text{Cl}$ ,  $\text{CH}_3$  and  $\text{HCl}$ . Similar studies were done by these workers [47] for several engineering thermoplastics such as polyetherether ketone, polyethylene terephthalate and polyethylene sulfide.

### **8.31.2 Biodeterioration**

Flame-retardant and oil/water-repellent Nylon is used as an outer layer of special combat clothing for the defence services. A treatment of thiourea-formaldehyde and fluorocarbon polymer finish (FC) imparts flame retardancy (FR) and oil- and water-repellency to the Nylon substrate. Biodeterioration of FC-FR Nylon was studied by Setua and co-workers by soil burial, air exposure and immersion in a standard culture [48]. It was observed that in all the modes of exposure there was a reduction

in physical properties. Oil- and water-repellency and FR were adversely affected. The most severe damage occurred by degradation due to soil burial. A comparison of the TGA plot of control and soil burial samples showed a lower decomposition temperature of the latter, presumably due to the decomposition of the thiourea-formaldehyde resin coating. Base Nylon fabric also showed degradation upon soil burial. Scanning electron microscopy showed complete deterioration of the coating material with formation of debris.

## **8.32 Resistance to Penetration or Permeation of Chemical Warfare Agents: Defence Applications**

### **8.32.1 Introduction**

These tests are for evaluating protective clothing against chemical warfare agents that manifest their effect by absorption through skin (e.g., vesicant and nerve agents). The tests described in this section have been compiled from the TNO Netherland report by Oudmaijer and van Eenennaam [49]. The report contains a range of test methods to determine chemical and biological protection as well as protection against flames and the thermal effects of a nuclear explosion provided by a nuclear, biological and chemical (NBC) clothing ensemble [49]. These test methods have been adopted by many countries with modification to suit their specific requirements.

Coated fabrics are used for protection against chemical warfare agents, so test penetration by these agents only have been discussed in this section. A chemical warfare scenario in the battlefield is discussed for better appreciation of the methodology adopted for a particular test.

#### **8.32.1.1 Chemical Warfare Scenario**

In a battlefield, liquid chemical warfare agents are usually dispersed in the atmosphere by bombs, rockets or by spraying from tanks and aeroplanes. The droplets fall down due to gravity. Their speed is dependent upon frictional resistance by air and their size. The size of the droplet depends on the physical characteristics of the agents. The type of agent and its size and energy (falling or touched on a contaminated surface) are important parameters in the choice of the test. TNO has described different laid droplet tests to mimic the following conditions [49]:

- Handling of contaminated material and decontamination (Section 8.32.2).

- Contact with a contaminated surface (Section 8.32.4.1.1).
- Fallen drops to mimic the impact of droplets on protective clothing (Section 8.32.4.1.3).
- Wearer of protective clothing may kneel or crawl on a liquid contaminated surface, resulting in spreading and increased penetration. The pressurised laid droplet test is used to mimic such a situation (Section 8.32.4.1.2).

The impacted liquid droplets will eventually evaporate due to temperature and wind. The evaporated liquid will form a vapour cloud which will be transported by the wind. Protective clothing has, therefore, to offer protection against vapour challenge. Vapour challenge tests are done by blowing contaminated air with different wind velocities and challenge concentrations on the protective clothing. The standard agent used for tests is sulfur mustard. Soman is used as a representative of a medium-volatile nerve agent.

### ***8.32.2 Qualitative Liquid Mustard Agent Penetration for Air-impermeable Fabric***

This test is for impermeable fabrics that are subject to liquid contamination because these materials are meant to protect against the severest challenge of liquid agents [49]. Penetration of a liquid agent through impermeable materials occurs by permeation through the material and penetration through the seams. Change in colour of a detection paper is noted to observe these local penetrations and the time in which the agent reaches the other side of the material.

The test aims to saturate the sample locally by means of a liquid agent. The size of the cell and quantity of the agent is not important as long as saturation is reached. A specimen is placed in a cell. A 1.5 cm<sup>2</sup> piece of filter paper is placed on the sample and is contaminated with 50 µl of mustard agent by means of a dispenser. An inverted petri dish sealed with wax is placed on top of the cell to prevent evaporation of the mustard agent. Underneath the cell, a detection paper made of Congo Red paper with tiny drops of chloroimide is placed in contact with the test specimen. The cell is placed in a thermostatted cupboard and the detection paper inspected at regular intervals. The time of appearance of blue dots on the detection paper is noted, and the result expressed as the BTT in hours.

### **8.32.3 Testing of Permeable Clothing Against Gas Vapour of Chemical Warfare Agents**

This test is for vapour challenge of permeable clothing [49]. The test determines the BTT of the clothing, using realistic dosages of the agent and realistic air flow (convective flow) through the clothing ensemble.

The testing equipment contains a generator part and a challenge part (**Figure 8.8**). In the former, nitrogen flow is passed over a glass reservoir filled with the agent. Evaporation of the agent is controlled by temperature and nitrogen flow rate. For mustard agents, the concentration choices are 11 mg/m<sup>3</sup> or 20 mg/m<sup>3</sup> at a simulated wind velocity of 5 m/s, and 55 mg/m<sup>3</sup> at a simulated wind velocity of 1 m/s. For Soman, these are 20 mg/m<sup>3</sup> and 66 mg/m<sup>3</sup> for 1 m/s and 5 m/s wind velocity, respectively. The nitrogen-containing agent is then blown into a thermostatted exposure vessel at 30 °C, and 80% RH. Twelve samples can be tested simultaneously in the chamber.

The sample is fixed in a sample holder with an area of 12.6 cm<sup>2</sup> which is connected to the exposure vessel. Bubbler are connected to the testing cell. During the test, air is sucked through the test sample. The air flow depends on the air flow resistance of the complete assembly mimicking a realistic wind velocity of 1 m/s or 5 m/s perpendicular to the sample. The flow rate is calculated from **Equation 8.3**:

$$F = V_w^2 0.057 / R_{\text{clothing}} \quad (8.3)$$

where F = flow rate in cm/s,  $V_w$  = wind speed (1 m/s or 5m/s), R = air resistance or pressure drop at a flow rate of 1 m/s expressed in mm water [mm water/(cm/s)], and 0.057 = a constant related to wind velocity normal to the fabric face.

The agent penetrated through the clothing material is collected in diethyl succinate and the total amount is determined by gas chromatography with flame ionisation detection (GC/FID). The result is presented as mg/min/m<sup>3</sup>. The challenge concentration, the flow rate through the material and time are stated. From the data obtained for a specified period of time, the protection offered by the clothing is judged.

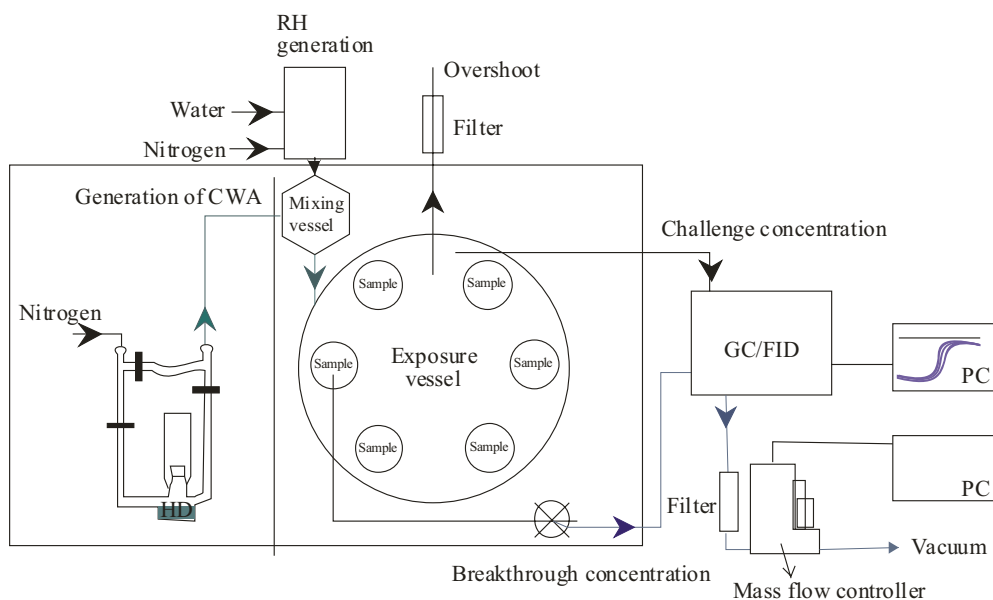


Figure 8.8 Vapour testing equipment (schematic)

#### 8.32.4 Liquid Tests for Permeable Clothing

Liquid tests are carried out in two stages. The first stage is application of droplets on the sample. These may be laid droplets (contact), pressurised droplets (crawling), or falling droplets (see Section 8.32.1). The second stage is exposure which may be flow drawn through the material (convective flow) or without flow through the material (diffusive flow) [49].

##### 8.32.4.1 Application of Droplets

###### (a) Laid Droplets

Droplets of the agent are, in general, laid onto the sample by means of a calibrated syringe-dispenser combination. The regular size for neat agent is a 1  $\mu\text{l}$  droplet. Thickened agents are placed by calibrated pipettes (30 mg are usually employed). For the diffusive flow test, TNO describes eight 1  $\mu\text{l}$  laid droplets of neat mustard on a 10  $\text{cm}^2$  cell or by 1  $\mu\text{l}$  of neat mustard on a 1.5  $\text{cm}^2$  cell. For convective flow, ten 1  $\mu\text{l}$  laid droplets of neat mustard agent or twelve 1  $\mu\text{l}$  Soman droplets are

placed on a 12.5 cm<sup>2</sup> cell. For thickened agents, one droplet is placed per cell, the size of which is chosen by the customer.

*(b) Pressurised Laid Drop Test*

After application of the laid drop as shown previously, a pressure of 200 kPa is applied statically for 5 minutes to mimic crawling. The test is usually done using 30 mg of thickened mustard and pressure applied by placing a weight on the drop.

*(c) Falling Drop Test*

The sample is placed in a 1.5 cm<sup>2</sup> cell and 1 µl of neat mustard allowed to fall on the specimen from a height of 2 m. Exposure of the fallen drop is done by the diffusive flow method. For thickened agents, the sample is placed on a cell of 19.8 cm<sup>2</sup>, and 5 mg or 30 mg of thickened mustard is allowed to fall on the sample from a height of 7.5 m.

#### **8.32.4.2 Exposure**

If the clothing is tight to the skin and the air flow rate is low (0.2-0.5 cm/s), the agent will enter the protective clothing by diffusion. Diffusive flow is obtained by using a low wind speed and placing a polyethylene membrane underneath the material in the sample cell. Another way to mimic diffusive flow is dual flow, in which air is passed on top and underneath the sample at an equal flow rate. Both methods are used for testing.

At high wind speeds and if the clothing is not in close contact with the skin, wind enters perpendicular to the surface of the protective clothing, i.e., convective flow occurs. Convective flow is obtained by drawing air through the material. The flow rate at which air is to be drawn depends on the wind speed to be simulated and the air resistance of the clothing.

*(i) Diffusive Flow Using Polyethylene Film*

A protective clothing system is placed in a testing cell with a 10 µm polyethylene film directly underneath the sample to prevent air to flow through the material. The sample is then contaminated as described in **Section 8.32.4.1** and placed in testing equipment. Air at 30 °C and a velocity of 0.5 m/s is drawn over the surface of the clothing. Airflow of ~ 6 l/h is applied underneath the sample. The RH is <5%. The duration of the test is 24 hours. The mustard agent permeating through the sample is collected in diethyl succinate and the total amount determined by gas chromatography with a flame photometry detector (GC-FPD). The result is

expressed as the BTT in  $\mu\text{g}/\text{cm}^2$  for the specified challenge concentration for 24 hours.

*(ii) Diffusive Flow Dual Flow*

The sample is placed in a cell of  $12.6\text{ cm}^2$  area having a provision of air flow above and below the cell. The sample is then contaminated as in the procedure described in **Section 8.32.4.1** and placed in testing equipment. The flow of air above and below is set so that there is a negligible pressure drop across the sample to prevent flow of air through the material during the test. TNO specifies 250 ml/min of air at a velocity of 0.1-0.2 m/s above and below the sample at 30 °C and 80% RH. The test is carried out for 24 hours. After the test period, the permeated agent collected in diethyl succinate is analysed by GC/FPD. The result is expressed as  $\mu\text{g}/\text{cm}^2$ .

*(iii) Convective Flow*

In this test, air is sucked through the sample material to simulate convective flow. The sample is placed in a cell of  $12.6\text{ cm}^2$  area and contaminated with the liquid agent as described in **Section 8.32.4.1** and placed in an exposure cabinet. Tubes on top of the cells provide laminar flow on the cell surface. Under the cell, a bubbler filled with diethyl succinate is connected. Air is sucked through the test sample to simulate convective flow of 5 m/s. The temperature and RH are set at 30 °C and 80%, respectively. The duration of the test is 24 hours, after which the permeated agent in diethyl succinate is analysed by GC-FPD. Results are expressed in  $\text{mg}/\text{min}/\text{m}^3$ .

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# 9 Quality and Productivity Improvement in Rubber-coated Textile Industries, Tools and Techniques

**Bireswar Banerjee**

## 9.1 Introduction

The concept of quality first came into use during the Industrial Revolution. Initial models of quality improvement processes date back to the early 1900s, but progress in the methodology of quality development was observed only from the middle of the 20<sup>th</sup> century.

Shewart of Bell Telephone Laboratory in the USA first applied a statistical quality control (QC) chart to manufactured products in 1924, and this may be considered as the first step towards the modern system of quality management.

Pioneering leaders such as Frederick Winslow Taylor, a mechanical engineer, realised that management should accept the responsibility for planning and organising work, evaluating work and the management thereof in a 'scientific' manner. The American automobile industrialist Henry Ford led the way in measuring the quality of output.

The Taylor system was introduced in the early 20<sup>th</sup> century. It was responsible for virtually all planning for operations and quality. Quality engineers' functions were associated with product quality in the factory, and reliability engineers' functions were associated with product quality in the field.

QC activities became significant from the 1940s to the 1960s. A growing perception of quality engineering emerged in the 1970s and that of management in quality systems emerged in the 1990s. Nowadays, quality management is a recognised and important profession within industry.

Ishikawa is recognised as the father of 'quality circle' (the Japanese method of quality improvement). He started working on QC in 1949 in Japan and led the Japanese quality revolution. In 1943, Ishikawa invented the 'fishbone' diagram, most likely the best known of all problem solving tools. The quality circle method was developed

by him in the 1950s when it was observed that American-style management was not very effective in Japanese industries [1].

Masaaki Imai introduced the 'Kaizen', the Japanese competitive success procedure. He studied American management practices in Washington. He introduced them to Japan in 1957, and introduced the concept of Kaizen in 1986. He defined Kaizen as a means of continuing improvement in personal life, home life, social life, and working life.

In the 1960s, the method 'Poka-Yoke' was invented by Shigeo Shingo of Japan. It translates as 'prevent inadvertent mistakes'. It has incorporated error-proof techniques into a remarkable tool to achieve zero defects. The perception of zero defects first originated in 1961 in the Orlando Division of the Martin Company in USA, which manufactured missile systems [2].

Quality circle was introduced in California, USA, during the mid-1970s. For the implementation and advancement of QC, training courses, conventions, and published materials have been developed.

In the 1980s, Juran, a pioneering expert in quality planning, discussed the importance of planning for quality. The concept of defect free output or zero-defect products and the quality which can be achieved without cost has been reviewed by Crosby who claims that 'quality is free' [3].

The business management strategy - Six Sigma originally developed by Motorola (USA) in 1981 has widespread application in many sectors of industry. The particulars of its methodology were formulated at Motorola in 1986. Six Sigma is a process which identifies the imperfections and flaws within the working system and processes of the organisation.

Quality methodology is significant throughout an enterprise from corporate objectives to individual objectives. Total quality shows the way to improved productivity, increase profitability, and provide greater motivation for all the people in an organisation.

## **9.2 Global Competitiveness**

To survive in the current global competitive scenario, the existence of rubber industries depends not only on its present infrastructure, brand image, product quality, price, product differentiation, and present market status, but also has total commitment to improve continually in all its processes (especially in its core processes, which envisage the customers). To achieve excellence in global competitiveness means utilising quality tools [4].

### **9.3 Total Quality Management for Rubber Industries**

Towards the ultimate aim of entire customer satisfaction, the total quality management (TQM) (which is a scientific approach towards continuous improvement involving everyone in every function of the organisation) has to be implemented in every facet of operations. The significance of TQM and quality improvement is not only important to the industries themselves, but ultimately to society as a whole.

The definition of TQM as specified by the International Organisation for Standardization (ISO) is 'TQM is a management approach for an organisation, centred on quality, based on the participation of all its members and aiming at long-term success through customer satisfaction, and benefits to all members of the organisation and to society' (ISO 9000:2005) [5].

The most widely recognised international standard for Quality Management is ISO 9001:2008 (the latest version of the Quality Management System of ISO). Companies who have already implemented and registered with this management system can introduce TQM for execution of management orderliness to maintain and improve the quality of their products.

The first step for business excellence is to frame TQM. It is the foundation of all other concepts. These are; (i) customer focus (ii) competitive quality (iii) continuous improvement (iv) cross-functional team and Quality Circle (v) business process quality management, and (iv) partnership with suppliers.

The basic ideas of quality management work only if the workforce is properly trained and are clear about their assigned jobs. The employees at the grass-roots level will need to carry out the actual work whatever the management system (e.g., ISO 9001, Five S, Kaizen, Poke Yoke, or Six Sigma). Hence, if the workers are not enlightened, nothing will be successful.

In the present business world, quality means not only the product quality but the cost of a product, delivery schedule, and after-sales service is also included with it [4].

TQM is a journey towards excellence. The management actions are:

- Constitute a Quality Council.
- Education and training for all.
- Deployment of annual quality goals.
- Planned processes to meet goals.

- Measurement of feedback and audit.
- Recognition and reward.

TQM is considered to be in the category of a planned top-down move towards change. TQM is an extensively used approach for advantageous organisational agility and enhancing employee commitment to change. TQM programmes typically have the following elements [6]:

- Problem solving attainment involving workplace employees on a continuous basis.
- A quality structure to focus the process (usually through direct finding groups).
- Measurement of quality using statistical methods.
- Identification of customers (internal and external).
- Extensive training on a regular basis.

### **9.3.1 Managing Quality in Rubber Industries**

The first step for business excellence is to frame TQM. It is the foundation of all other concepts, these are;

- Customer focus.
- Competitive quality.
- Continuous improvement.
- Cross-functional team and Quality Circle.
- Business process quality management.
- Partnership with suppliers.

The testing of the physical properties of the rubber and the textile used in any application is critically important for the design, manufacture, quality assurance, and product performance during the service life of a rubber/textile composite. The manufactured product of rubber is a highly complex material composed of a combination of properties. The different types of rubber compounds processed every day by a rubber processor exhibits individual physical characteristics.

With so many variations in compounding and processing, it is all the more difficult to control. If an operator of a rubber processing machine make mistakes, it is necessary

to check the batches in the process. Similarly, if a machine malfunctions it is important to examine its performance.

If a material does not conform to the specification or standards, it may be missed and the reason may not be found, so to 'do it right first time' is to avoid failure and to eliminate a recurrence.

In a rubber processing industry, the production process cannot be conducted efficiently without control in each and every raw material consumed for manufacture, testing of on-process material, and the final products. Some of the critical items made of rubber-coated textiles used in lifesaving devices and other safety items may be subject to destructive testing on collecting a representative sample from the bulk lot. Considerable cost saving can be established on testing of raw material and material on-process to prevent the use of non-conforming or low quality materials. Therefore, the quality measurement is the cost of non-conforming items because a rubber product is a complex and an unique engineering material.

### **9.3.2 Quality Policy**

Prior to the introduction of any quality planning, the management must frame a quality policy which is a documented procedure of strategic quality planning. This will serve to provide internal consistency to achieve the goal by bringing into line each member, department and the whole of the company in approaching its long-term objectives.

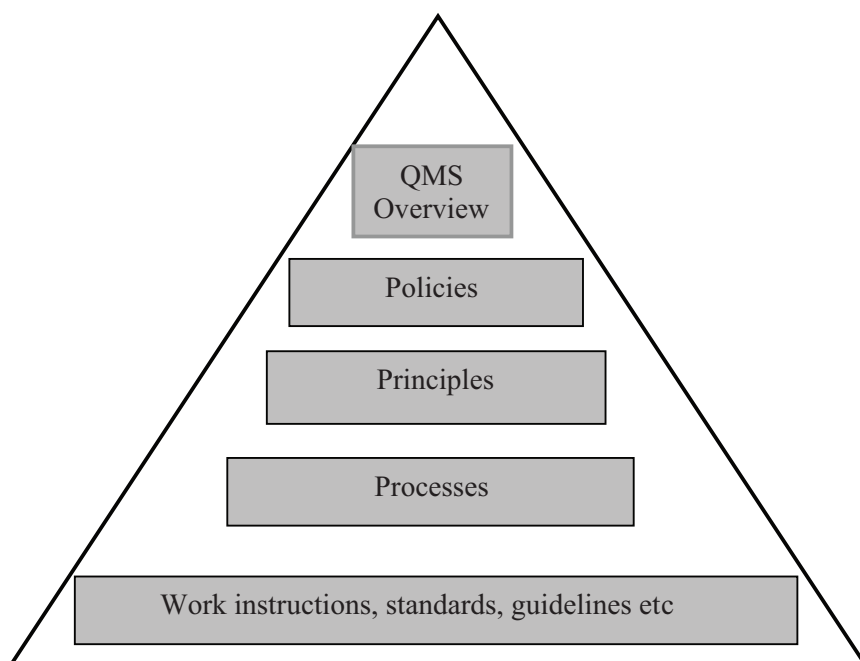
The effective policy documents have to encompass the following:

- The quality policy has to be in clear, brief and in explicit terms. Its policy once framed shall be circulated to all the employees and displayed at prominent places in the company.
- It must focus on meaningful and achievable targets. The policy must communicate the values and beliefs in the accomplishment of goals.
- It must be approved and signed by the head of the organisation, and all employees must abide by it.

Many companies have ambivalent attitudes towards their quality policies – they are prepared and displayed but not followed. In such situations, the policy does not reflect the true intentions of the top management; once it is framed the employees should believe in it for it to be followed properly [7, 8].

A quality management system (QMS) pyramid is illustrated in **Figure 9.1** [9].





**Figure 9.1** Quality management system pyramid

## **9.4 Objective-oriented Planning**

The Ziel-Orientierte Projekt Planung (ZOPP) approach is a group problem solving technique which has been promoted and used by a German Technical Cooperation. It can be represented in English as Goal-Oriented Project Planning.

### **9.4.1 Methodology of Ziel-Orientierte Projekt Planung**

ZOPP can provide a systematic structure for identification, planning, and management of projects such as quality improvement for rubber processors, developed again in a workshop setting, with principal interest groups. The effectiveness of ZOPP is in a planned setting: the project framework is reasonable. It recapitulates and puts together the main elements of a project and points out logical relationships between intended inputs, planned activities and expected results. The methodology provides an orderly structure for identification, planning, and management of projects developed again in a workshop situation, with principal interest groups.

The ZOPP has two initial segments: (i) analysis, and (ii) project planning. The analysis part consists of four subsections, with the identification of actual problems as a means to implement the protocols [10]:

- Participation analysis: a general idea of the company and people associated with a project and their attitudes and involvement for planning. This may be drawn in a chart.
- Problems analysis: identification of core problems. Major problems are to be noted and these problems can be identified with the help of cause-and-effect analysis.
- Objectives analysis: a restatement of the problems into pragmatically achievable goals.
- Alternatives analysis: identification of objectives and assessment of alternatives according to resources in achieving objectives, cost-benefit ratio, sustainability, and others factors as decided by the group.

This may be prepared on charts, and develops and assesses alternative or competing strategies to achieve the agreed objectives in an efficient way [11].

#### **9.4.2 Participation of Employees in the Planning Process**

The application of ZOPP in the quality planning of a project actively involves the people affected by the project in the planning process. This may be geared up by inviting all relevant employees to participate in the respective planning and by conducting workshops on quality improvement. The plan must be approved by all interested employees and they are to be included as participants in the planning process. The important management task is to guide this planning process.

The ZOPP approach provides tools that are vital to achieve teamwork in groups, visualisation of the discussions, and documentation of the results. It is a powerful tool for integration of experience, proficiency and knowledge of senior management.

## **9.5 Quality Management Tools**

Well-recognised quality management tools are readily available.

### **9.5.1 Quality Improvement Techniques: The Five-S Programme**

The simple, widely practised tool Five-S refers to the five Japanese words: seiri, seiton, seiso, seiketsue, and shitsuke. It is found to be very effective and successful for the management of housekeeping, productivity and ultimate quality of products in different countries. These first step management tools are easy to implement, and may be practised on the shopfloor without adding any extra cost to the product for workplace management [12].

**Seiri** means ‘organising’ or ‘re-organising’, distinguishing between necessary and unnecessary things. Keep those materials, dies, tools, and equipment which are needed and discard those which are unnecessary. It involves differentiating between wanted and unwanted items. Upon practising this, additional space can be made available, things can be easily identified and accessible, health and safety issues can be addressed, and the inventory can be reduced.

**Seiton** means ‘neatness’. Everything is arranged in an orderly manner. A system to be established to return each item to its proper place, such as tools, fixtures, and equipment, will help to cut down time in searching for materials. The premise should be ‘a place for everything and everything in its place’.

Floors should be kept clear and clean with bright colour markings dividing them into sections. Identify the work area, storage area, finished products space, and lanes for movement. This practice will create a working environment which is effective, safe, interesting, and also assist in inventory control, and overall proper utilisation of the workplace.

**Seiso** suggests ‘take up the job cleaning or shining’. Always keep the workplace and environment clean. This cleaning is not restricted to the machine, shopfloor or working areas, but should be extended to the entire surroundings for the management of a clean and healthy atmosphere. Inspection and cleaning on a regular basis will help to make easier identification of defects in the machine, equipment, tools, working areas, as well as safety. Regular inspection may detect leakage, unusual noise/vibration of the machine, missing tools, breakage, availability of materials in the workplace, and help to organise all cleaning aids.

**Seiketsu** suggests 'systemising practices'. Standardising or maintaining what has been achieved in the three good practices mentioned previously which can be introduced but may be difficult to maintain. To sustain the system, it has to be standardised to maintain the cleanliness obtained on a permanent basis. A regular routine system as converted into a regulated procedure and turned into a habit.

Communication channels are formed between the management and the shopfloor/workplace through a visual control system. Hence, everyone knows about the process changes in day-to-day activities in running the plant/workshop, which will improve work efficiency.

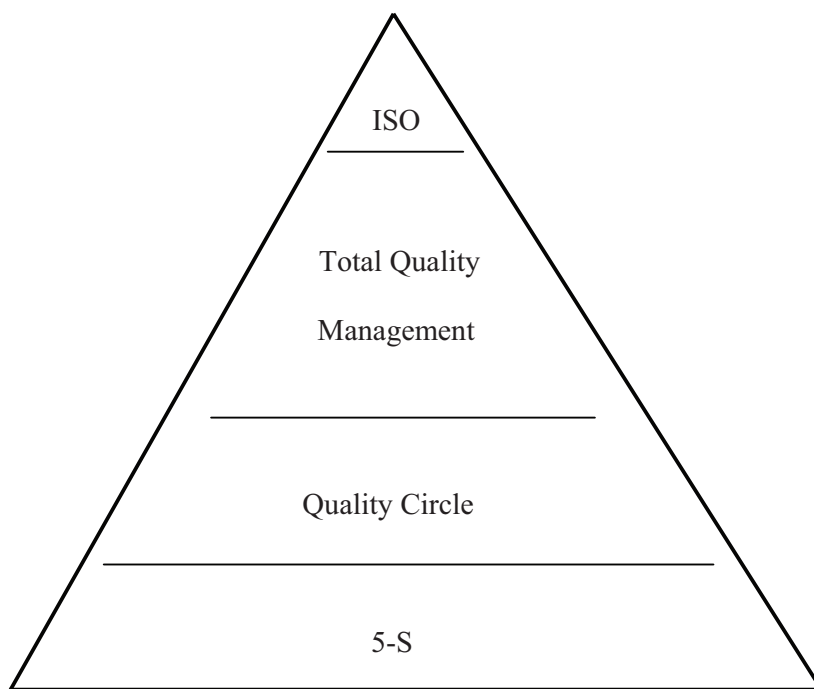
Visual management involves displaying instruction charts, name of equipment, date of preventive maintenance, cautions, danger alerts in a proper place, and following up the instructions. This will synchronise the three activities mentioned previously and help in reducing defective production and machine breakdowns.

**Shitsuke** means 'self-discipline'. Be disciplined – follow procedure, set-up 'standards' and ensure that they become a discipline and way of life for everyone in the company. These may already be in practice but without any significance attached to them. Training is to be organised in a manner so that everybody can participate.

It will be very effective to use '5-S' posters and signs prominently at shopfloors. It is necessary that everyone in an organisation understands them clearly and the best way of doing it is engaging everyone, and it will require a little time.

A formal monitoring/follow-up system should be established for an overview of the development programme to ensure 5-S discipline becomes a way of life [6].

The level of QC pyramid is shown in **Figure 9.2**.



**Figure 9.2** Levels of quality control

## **9.6 Lean Manufacturing Method**

The Lean production system was developed and introduced to automobile manufacturers after the Second World War. Lean, a familiar word in the current industrial world, arrived from the ability to accomplish more with less resources by the continuous elimination of waste.

‘Lean’ signifies a logical move towards ascertaining all types of wastes and best possible management of resources, incessant improvement, and ensuring smooth flow of the product in the supply and manufacturing sequence to meet customers’ requirements. It is a method of doing more with a smaller amount of inventory, minimum time, less space, smaller workforce and fewer costs.

A quality product can be produced on monitoring the Lean speed by ‘doing a job right first time’. A lean way of thinking also supports growth by improving productivity and quality, reducing lead times and reducing an inventory of raw materials.

A highly evolved method emerges out of the Lean thinking on managing an enterprise. That is, efficiency and effectiveness to improve productivity and quality of product; predominantly effective during an economic downturn.

### **9.6.1 Lean Manufacturing Principles**

There are five basic approaches in a Lean manufacturing process:

- Identify what creates value from the customer's perspective.
- Make all the steps across the whole value stream.
- Make those actions which create value flow.
- Only make what is attractive to the customer 'just in time'.
- Strive for perfection by continually removing successive layers of waste.

### **9.6.2 The Seven Wastes**

In an organisation, for example a rubber processing unit, which is an intensive labour- and power-consuming industry, seven categories of wastes can be identified in a Lean manufacturing study which costs the manufacturing company without any value addition to a product. In addition to those seven categories, there is one which is recognised as the most irreconcilable waste:

- Overproduction: overproduction and early production involves producing more than the customer has asked for, or providing unordered products.
- Waiting: idle time created if material, information, operators, or equipment is not ready: time when no value is added to the product.
- Transporting: movement of information, people, or materials that does not add value.
- Over-processing: efforts that add no value from the customers' viewpoint.
- Excess inventory or work in progress: more information, projects, material on hand/waiting than can be worked on, or which the customer requires immediately.
- Ineffective motion: unnecessary movement of workmen during the process of the operation that does not add value to the product.

- Product defects: products with defects that require rework, repair, return by the customer. This costs the company.
- Under-utilisation of employees: workers who are under-utilised due to lack of proper training for work and not motivated can be considered to be an additional waste, adding item 8 to the original 7.

By capitalising on the employees' capability and creativity, a manufacturing company can remove/reduce the other seven wastes, and may improve their performance continuously [13].

## 9.7 The 3-M Practice

The practice of three Japanese magic words, muda, muri and mura, in the workplace will bring down the cost of production without affecting the quality of the ultimate product. Processing by a rubber product manufacturer involves passing through a series of stages from input of raw materials to the finished product and finally its packaging and shipping. Value is added to the product at the end of each process, and it is sent for the next procedure of the operation.

At every stage of the production process of a rubber-/textile-coated product (especially large fabricated and assembled engineering structures), there is a need for careful observation and critical testing to ensure the satisfaction of the next internal customer and to offer a quality finished product to the ultimate user at an appropriate cost.

**Muda** means 'waste'. This is an activity that does not add value but includes the total cost of product failure plus the cost of internal failure in addition to the cost of various preventive measures. Proper corrective and preventive actions must be taken upon identifying and analysing the wastes. This will help to increase productivity, reduce the total cycle time of producing a product, and overall reduces the cost of production, ultimately providing satisfaction to the customers.

**Muri** means 'excessive strain', an unreasonable approach to any field of operations. Identify and eliminate the things from the activities which are extremely difficult to carry out. Activities which are unnecessary, or which impart no benefits, should be eliminated.

**Mura** means 'discrepancy', actions which are irregular, uneven or inconsistent. An effective improvement tool calls for elimination of inconsistency in areas such as men, method, manufacturing equipment, and materials. The discrepancies should be identified, analysed, and eliminated to remove inconsistency to lead to a continuous improvement process.

It may be the tendency of people to deviate from the laid-down standards, resulting in variability in actions and generation of wastes. Deviation of the product or services should be at the lowest level between the acceptable and non-acceptable [14].

## **9.8 Quality Circle in the Success of Total Quality Control**

The Quality Circle consists of a group of workmen from the same working area voluntarily forming an application group, meeting at regular intervals to study, identify, analyse, and solve quality-related problems. It is a people-building philosophy, providing a holistic opportunity for the development of an individual by self-development, mutual education, and continuous activity.

The foremost aim of the Quality Circle is self-development and mutual development of grass-roots level employees. Its basic concept is the prevention of a problem, not solving a problem. It can be carried out anywhere in the world and in any kind of establishment.

The participants in a Quality Circle need independence and individual development. It is also desirable for the Quality Circle to leave out managerial personnel in the activities otherwise the members will be dependent on them. Initiative and improvement offered by the members are likely to be inhibited. However, it is necessary to get support and counselling from the executives as and when required. Such an approach will help to develop the performance of the Quality Circle under the guidance of a Facilitator who is a nominated manager to catalyse and stimulate the Quality Circle [15].

A feeling of solidarity among workers will accrue on their involvement in Quality Circle activities, and they will also realise that QC makes sense.

It may also be reiterated that the 'Japanese economic miracle' is not associated with one thing, but has been generated from various improvement schemes. There was a common feeling from managers from other countries that Japanese economic success was due only to certain techniques. However, this is not correct, it has been achieved based on the foundation of many quality improvement ideas, including the Quality Circle [16].

### **9.8.1 Quality Circle Tools**

There are seven basic tools employed by the Quality Circles and the management in problem solving techniques for the activities of quality improvement:



- Brainstorming – collective thinking power of a group of employees come up with ideas which can be evaluated in identifying problems, analysing the cause and highlighting potential solutions to the problem.
- Data collection – this is the process of collecting the required information in figures by the group. These data are useful for statistical analyses of a problem, and may assist in taking decisions concerning corrective actions.
- Analysis or stratification of data – by this method the team analyse and classify the probable causes of the problem. It is a process to separate data into categories. It is normally done for identifying the groupings responsible for the difficulties being encountered.
- Pareto analysis – the Pareto diagram is a technique to concentrate attention on the few important problems and arranging data according to priority or significance. It can then be used in a problem solving process.
- Cause-and-effect analysis – the probable causes of defect of a process/product may be due to one or more reasons. A systematic diagram can be drawn by planning out all the probable causes to find out the relationship between the cause and effect.
- A typical model of cause-and-effect analysis is portrayed in **Figure 9.4** [15].
- Histograms – variations in a process or product can be summarised in a graphical depiction of frequency distribution by preparing a histogram.
- Control techniques – this is a graphical representation method to assist process control. There is a central line and two limit lines on either side of the central line: ‘upper control limit’ and ‘lower control limit’. Quality measured at different times is plotted on the chart, and the efficiency of control can be evaluated.

Quality Circle activity can be successful because of a system of mutual encouragement and exchange of views; when the Quality Circle movement was initiated in manufacturing activities, its substantiation was inspiring. In Quality Circle activities, every one could participate and contribute to improvements. There is no discrimination with regard to the job of a worker, if it is carried out well, it may influence co-workers to join in the activities [1].

A comprehensive model of Quality Circle events is shown in **Figure 9.3** [1]

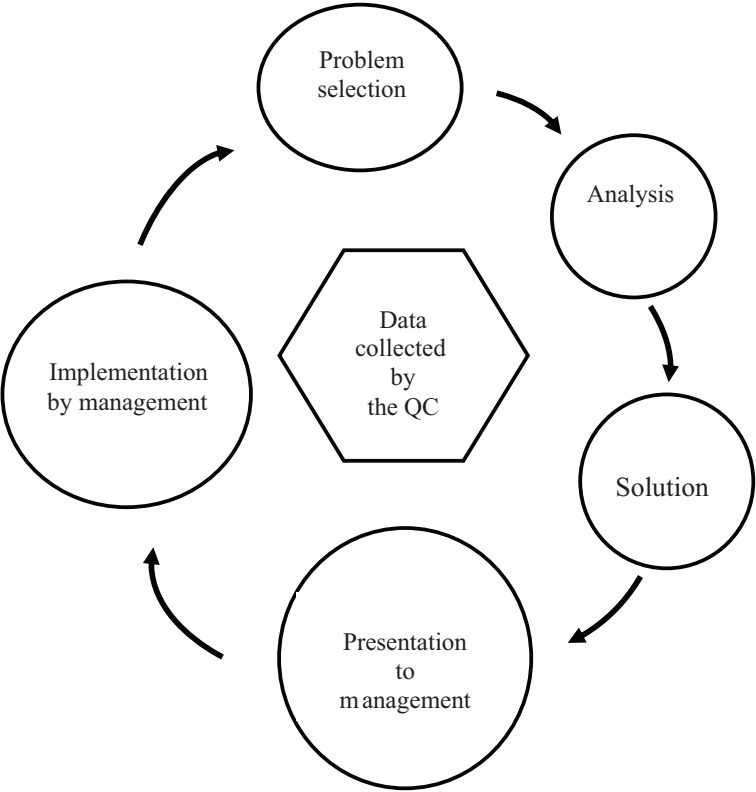


Figure 9.3 Quality Circle Activities

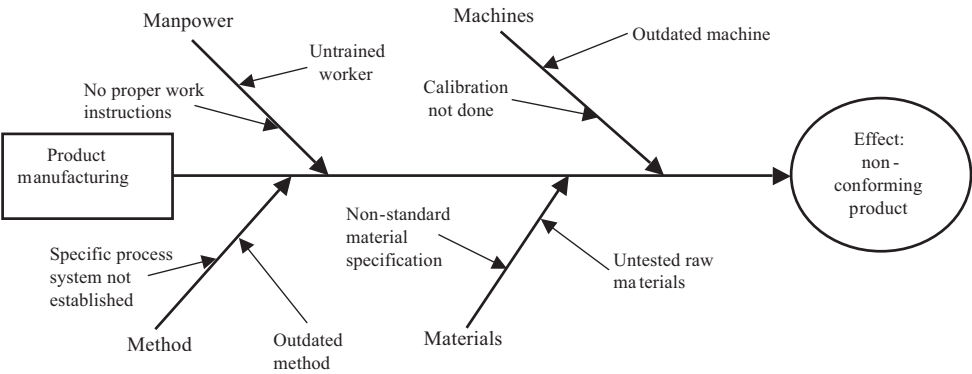


Figure 9.4 Analysis of cause and effect

## **9.9 Kaizen the Continuous Improvement**

‘Kaizen’ means ‘continuous improvement’, the introduction of which in Japan’s industries resulted in elevation towards an industrial and economic power. During a period of crisis, Kaizen transformational change works well if major changes are required to ensure survival of the enterprise. When selecting an organised quality improvement programme, all the aspects of quality should be taken into consideration. Kaizen is considered to also cover Total Quality Management, and overlays all the events of continuous improvement.

There should be unending improvement to get advantages against competitors and to survive in business. There are two major activities in Kaizen from the management point of view: improvement and maintenance. Improvement is the responsibility of top, middle and supervisory levels, and maintenance is the equal responsibility of supervisors and workmen.

### **9.9.1 Relevant Factors in a Manufacturing Industry**

The main factors which need to be established in an industry for gradual improvements are:

- To establish a favourable environment and encourage continuous improvement in technological, managerial and operational activities, and to set standards.
- Ascertainment in maintaining standards.

In the maintenance function of Kaizen, the tasks of management are:

- Frame policies and procedures.
- Establish standards.
- Ensure that standards are adhered to by all.
- Evaluate and monitor improvements.
- Educate and train employees to facilitate them to follow the standards with an emphasis on the implications of following them.

Standards are not invariable in Kaizen. While they are to be maintained, they can be replaced by new standards as a function of continuous improvement, one following the earlier one. Although maintenance of standards contributes a vital part in workmen’s

functions, they are also expected to suggest small, developmental changes in support of continuous improvements.

The development processes in Kaizen are people-oriented. They provide an opening for the participation and involvement of workmen through the creation of an advantageous environment by providing education and training, which increase confidence.

In a result-oriented world, thinking for progress to achieve results is important. However, for Kaizen it is different, requiring continuous improvement, so to focus on people is particularly imperative.

### **9.9.2 Process-oriented Perspective**

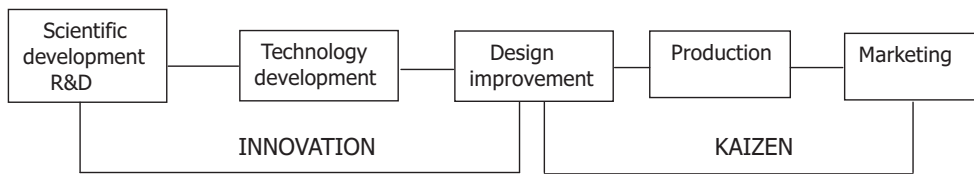
The process-oriented perspective is for the long-term, whereas the result-oriented approach is for the short-term. People-oriented Japanese perceptions are all process-oriented. Managers' concerns for process- and people-oriented approaches should focus on the following:

- Discipline
- Management of time
- Skill development
- Participation and involvement
- Augmentation of people's morale
- Two-way communication

It should be understood how Kaizen is different from innovation in the total manufacturing sequences. Nevertheless, the two courses of action, innovation and Kaizen, can be functional at every stage in the manufacturing process. In the normal situation, these two manufacturing sequences are applied at two distinct stages in each.

Innovational effects can be observed in the region of technological developments leading to new proficiency; and afterward to proceed in that direction. However, the impact of Kaizen can be observed more in the areas of production leading to customer satisfaction [17].

An illustration of innovation and Kaizen is shown in **Figure 9.5** [17].



**Figure 9.5** Innovation and Kaizen

### **9.9.3 Implementation of Kaizen as Continuous Development**

Within the working environment the Kaizen application allows continued improvement involving everyone from managers to workmen equally. The business approach of Kaizen is to have everyone in a company working together to make improvements with sizeable capital investments.

The related outlooks with Kaizen are:

- Waste elimination
- Efficiency development
- Process improvement
- Increased morale

With the proper implementation of Kaizen the benefits are:

- Better utilisation of space
- Product quality improvement
- Effective communications
- Employee retention
- Better use of the company's resources
- Enhancement of production capacity

Kaizen's process-orientated method has to be applied first and results have to be achieved after that. It cannot be considered for short-term advantages. Sharing, caring and commitment are important on the part of management in Kaizen. It

can be measured from the point of view of employees' attitudinal change. Kaizen improvements have to be measured from the point of view of employees change for continuous improvement [18].

## **9.10 'Poka-Yoke' in Error-proof Product**

The term Poka-yoke is a Japanese word. It can be translated as 'Poka', meaning 'inadvertent mistake' and 'yoke', meaning 'avoid'.

Poka-yoke stands for 'mistake-proof' or 'fool-proof' and incorporates error-proof techniques into a formidable tool to achieve zero defects. Poka-yoke is a concept of preventing any defects (even a small number) from passing through the process to the next step of the operation. To compete with world-class manufacturing companies, the manufacturer adopts a philosophy and practice of producing a zero-defect product. This will call for systems that will help to immediately detect any error occurring in the process. Then the process can be corrected so that no defective material is produced.

Poka-yoke is not at cross-purposes with Six Sigma; knowledge of Poka-yoke is needed for Six Sigma teams if their project is concerned with error prevention, particularly in manufacturing activities, where mistake-proofing of the processes will result in zero error.

### **9.10.1 Poka-Yoke Manufacturing**

When Poka-yoke is introduced into manufacturing, it helps to build in quality into the process of manufacturing; it improves quality and reduces product defects. The key to successful business is to produce quality product by the company. Product defects arise during production process due to (i) process of manufacturing (ii) machinery used in processing (iii) human errors. It might be exasperating to a producer that customers demand zero-defect products.

In the situation of global competitiveness, manufacturing industries around the world make every effort to compete in the quality, reliability and cost of products. Inspection at every stage of production process and at its final stage of manufacture make the product costly.

Hence, incorporation of an error-proof system into the manufacturing progression helps to avert defects at all stages of production.

### **9.10.2 Sources of Product Defects**

Human error is the source of most defects in products. Similarly, in a rubber processing factory, persons responsible for chemical weighing may omit some chemicals; workmen in charge of processing may ignore processing instructions, resulting in incorrect processing. Sometimes an operator may mis-label the prepared compounds for further processing to be 'checked again' or 'reprocessed'; incorrectly labelled finished products may be sent to the customer. It is also found that in many cases operators are not aware that they are producing defective products for the internal or external customer.

This kind of non-conformity will arise if machinery is not set correctly, measuring tools (e.g., measuring balances/instruments) are not properly calibrated, or if outdated equipment and tools are used to carry out allocated work. To minimise or eliminate such non-conforming work, operators should be trained in the correct operational practices which they undertake. The effectiveness of training must be verified by their seniors.

### **9.10.3 Error-proofing Methods**

Poka-yoke is a technique to produce error-proof products in which inaccuracy may be caused by human error. Next, a few examples of Poka-yoke specifically for rubber and fabric-coating industrial operations are given:

- Identify materials by their characteristics such as weight, dimensions, design and colour. Establish a standard item as a good reference sample for comparison.
- Find out deviation from procedures, missing steps, and use of process sequence methods.
- Detect deviation from fixed values. Use instrumentation to measure the total length of the coated fabric, critical condition detection such as steam pressure, processing temperature, measurement of electric current consumed by machines, thickness, weight per square metre, and width of the fabric before and after coating.

Every employee of the organisation should work together to accomplish the goal of zero defects. The quality of the products starts from the product's design, and must be built into the manufacturing process. Each step of the manufacturing process must be evaluated by the Manufacturing Manager or quality personnel for potential human errors. Error proofing must be implemented to prevent human errors [5].

The method of Statistical Process Control (SPC), if implemented, assumes that 100%

inspection (which is a time-consuming task) is not necessary. SPC is a QC tool, not an error-prevention tool. It describes the process capability to produce good parts, but does not eliminate the source of defects.

## **9.11 Six Sigma Concept in Quality Management**

Six Sigma is an approach to business improvement that focuses on the decrease in variation in all work processes. Process variation results in unwanted side effects, including defects and incorrect operations. The world's leading manufacturing companies have adopted Six Sigma for business improvement.

This approach originated as a set of practices designed to improve manufacturing processes and eliminate defects, but its application was subsequently extended to other types of business processes. In Six Sigma, a defect is defined as any process output that does not meet customer (internal or external) requirement. Six Sigma was mainly instigated by established quality improvement methodologies such as Quality Control, TQM, and Zero Defects, which were institutionalised by quality management experts.

### **9.11.1 Six Sigma Methods**

Six Sigma methods and programmes are being used even at the stage of product development and designing of the services. Six Sigma is a process which identifies the defects and fault within the working system and the processes. It tries to reduce them to the minimum. It initiates goal defining, fault finding, performance measuring, and process controlling in a company. The object initially was to save cost but now it is to achieve the goal of elimination of all the possible defects from the organisational system.

The latest method is to bring together all elements of quality into one system under the practices of Six Sigma. It offers the perspective that the best approach is one that unifies all available quality tools to build a system of process improvement that drives out waste and incompetence by reducing non-conformities similar to the TQM system in a more scientific way.

### **9.11.2 Six Sigma Goals**

The principal motive is to make the company do extremely well in the products they produce and services they provide to the customers to meet extreme competitiveness.



The concept is based on customer contentment; it spells out the qualitative aspect of the system, and aims towards the best quality as far as products and services which are offered by the organisation.

Six Sigma involves seeking out the improvement procedure in process quality to obtain quality outputs by identifying and removing the causes of defects and reducing inconsistency in the processes of manufacturing. Familiarity with Poka-yoke is essential for the Six Sigma team members who are engaged in manufacturing areas for error prevention.

Six Sigma is not to be accomplished by inspection because it will add to the cost. At some point the need for Design for Six Sigma will be very clearly observable. The need to eliminate defect and errors at the root source through better processes and more efficient ways of handling and delivering will become clear. Hence, the perception of 'right first time and every time' will emerge. One does not inspect one way to Six Sigma but arrives at it by design provided the Six Sigma concepts are put into practice in the enterprise.

### **9.11.3 Implementation of Six Sigma**

Six Sigma is a highly statistical management tool, its customer receptiveness, and a profit-driven ethos are the benefits of the concept. That is its understandability and realisation of the need for implementing it in full in a company or in a section.

A Six Sigma vision statement is to be prepared by the top management in consultation with a Six Sigma consultant. There are no fixed formats or requirements for this. The top management should then make certain its farsightedness. They should make a decision to implement Six Sigma methodology which should percolate downward to the mid-level and operating stages. The Chief of Operations will specify where Six Sigma is to be initiated and what goals are to be accomplished in what time frame.

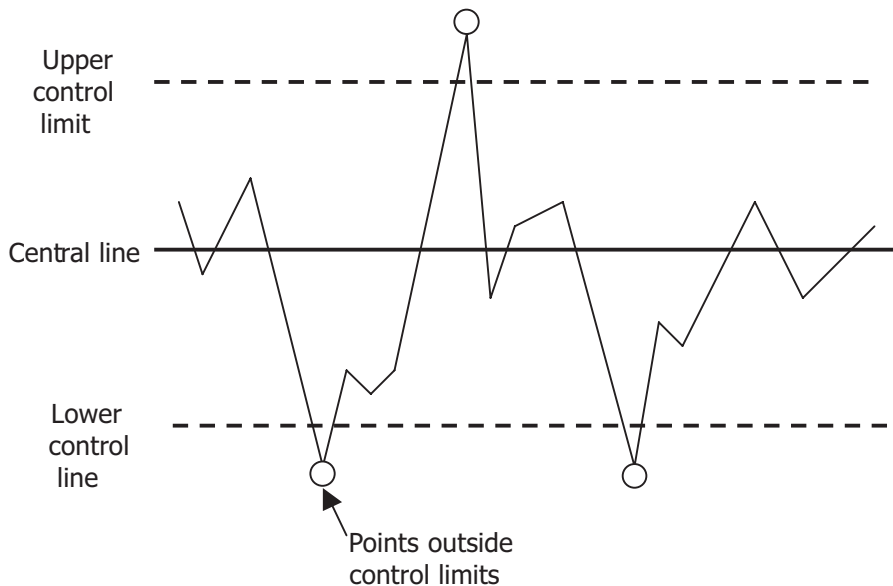
In achieving the success of Six Sigma methodology, the organisation should be positioned into a three-tier system of management (top, middle, operating level) and all the levels of management should be involved.

A set of quality management methods is utilised (including statistical techniques). A special team of people within the organisation (e.g., Black Belts, Green Belts) who are knowledgeable in Six Sigma methodological applications is created. A Six Sigma process is one in which 99.99966% of the products manufactured are free of defects, compared to a One Sigma process in which only 31% are free of defects [19].

A graph of control limits for process conditions is displayed in **Figure 9.6** [15].

The Six Sigma strategies corroborate with:

- Continuous efforts to achieve invariable and expected process results to minimise process irregularity.
- Manufacturing processes have a disposition that can be measured, analysed, transcended and controlled.
- Attaining continuous quality improvement needs commitment from the whole organisation, particularly from top-level management.



**Figure 9.6** Out-of-control process conditions.

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#### **9.11.4 Category Six Sigma of Belts**

In Six Sigma professional training there are four levels of Six Sigma belts. Each belt denotes the proficiency in that particular level:

- Yellow Belt is the lowest level in Six Sigma. The person trained at this level has basic knowledge about Six Sigma processes.
- Green Belts are the employees of an organisation who carry out Six Sigma as a part of their jobs. They generally assist Black Belts in collecting data and carry out various experiments as per the direction of Black Belts.
- Black Belts are the experts who are linked with measurement, analysis, implementation, and control segments. They identify the projects that can minimise consumption of material, labour input, cycle time and inventory. They apply the tools of problem solving techniques to the problem. Black Belts are designated and allocated full-time responsibility for the implementation of Six Sigma projects.
- Master Black Belt are the selected individuals who assist the champions in selecting projects (champions are Strategic Business Unit leaders who in sequence report to top management). They are senior professionals trained in advanced statistical tools and who work full-time on Six Sigma projects. They guide and follow-up a group of Black Belts. They select Black Belts and arrange training for them [19].

## **9.12 Zero-Defect Products as a Quality Goal**

Consideration must be given to the two principal meanings of ‘zero defects’:

- Defect free product (which is the literal meaning).
- A slogan to be used during campaigns in quality improvement.

A defect-free product has value as a long range goal because it signifies the need for never ending improvement. This concept discards the idea that perfection cannot be achieved. In contrast, if a defect free product is taken as a short-term goal, such a goal is in many cases not attainable. In such situations, the risk is that the dictat will be counterproductive by blocking efforts to reach achievable goals [3]. ‘Zero defects’ as a slogan means the term is taken up as a kind of banner to fly during a company’s campaign for augmentation of product quality.

The American use of employee suggestion schemes to improve product quality whether it is for internal customers or external customers has been altered in the Japanese system. The American style emphasises that suggestions are for economic benefits and proffer financial incentives, but the Japanese style places prominence on morale boosting of the employees that ultimately benefits all through positive employee participation. The effective Japanese system has to build up into two segments:

individual proposition and group suggestions (including those constructed by Quality Circles and Zero Defect groups).

Suggestion schemes are currently operational at most large-scale manufacturing companies and about half of small and medium-sized companies. According to Japanese companies' suggestion schemes, priorities are in the following order:

- Improvements in one's own work
- Savings in energy, material, and other resources
- Improvements in the working environment
- Improvements in machines and processes
- Improvements in jigs and tools
- Improvement in office work
- Improvements in product quality
- Ideas for new products
- Customer services and customer relations

Zero defects is a way of thinking, and the responsibility strengthens the idea that defects are not acceptable, and everyone should 'do things right the first time'. The conception of a philosophy of zero defects is that company's profits can be increased by eliminating the cost of failure and increasing profits through intensifying customer satisfaction. Zero defects is a motivation or a movement, it is not programmed, nor does it have distinct steps or rules to follow. Thus, the reason why zero defects can be effective in implementation in a company is that it can be acceptable to any enterprise [2].

### **9.12.1 A Proactive Approach**

Zero defects necessitates a proactive approach. Waiting for flaws to appear will be too late, hence the actions are:

- Zero defects shall be incorporated with the culture of the organisation. A Quality Improvement Team is to be created.
- Quality is to be built into performance expectations. Motivate the team members to think about how they can reach zero defects, and reward them if they are successful.

- Although zero defects are a destination, it should be appreciated that circumstances will keep changing. Analyse, assess, and adapt in a continuous process.

The four absolutes of quality management are:

- Quality is conformance to requirements
- Defect prevention is preferable to quality inspection
- Zero defects is the quality performance standard
- Quality is measured in monetary terms – the price of non-conformance.

### **9.12.2 Zero Defects Programme**

The stimulating feature of quality management could be specified by means of the relatively distinctive ideas provided by the Zero Defects Programme and Quality Circles. Conviction to zero-defect philosophy has faith in total achievement or ‘to do the job right the first time’.

Imperfection or errors are caused basically by two aspects:

- Lack of information
- Lack of attention

The corrective action for (a) can be taken by providing more information and knowledge, but (b) is an attitudinal problem.

Motivating the workers to gain pride in their jobs and to do their job as flawlessly as attainable the first time itself is the focal point of the Zero Defects Programme.

Motivation can be accomplished through: (i) displaying posters, (ii) publicity within the establishment, (iii) voluntary pledges by workers, and (iv) arranging visits of customers to the plant. Motivation should be with each worker to set up goals in the reduction of errors by himself, and the executives may help him in the performance.

Provision of knowledge should be provided about the product the worker is producing as well as where and how the item will ultimately perform. It is also necessary to instill an awareness of the functioning of the product quality to the workers involved. This kind of awareness campaign should precede the actual implementation of the Zero Defects Programme.

### **9.12.3 Implementation and Achievement of Zero Defects**

To achieve zero defects in a manufacturing organisation it is not just support, but active management participation that is the important requirement for success. A management standard to 'Do better work' creates an attitude of defect prevention.

Zero defects are the means for the management to utilise in explaining standards in a way that cannot be misinterpreted, and to be comprehensive about the particular culture of the company. Meticulous preparation is necessary before initiating any management programme, for instance: (i) celebration of Zero Defects day/week/month; (ii) awareness programme; (iii) error cause removal campaign; (iv) displaying banners; (v) posters; and (vi) handouts for employees.

It is consequently a motivational curriculum where workers are made more conscientious, more achievement-oriented and feel pride in their assigned work. Zero Defects Programmes cannot be a short-term programme, the objective has to be for a long-term agenda.

Recognition or awards to convince employees that the management is truly satisfied with their performance should be awarded with gratification and respect; their monetary value is not important.

Many in the manufacturing industries think that it is conceptually not possible to process zero-defect products. However, there are benefits which can be sought after the execution of this activity in terms of quality improvement and substantial cost-associated benefits with Zero Defects Programmes. In adding up the benefits in terms of better quality of product, there are many implied advantages:

- Better utilisation of the plant and machinery,
- Improved industrial relations,
- Gaining the loyalty of customers, and
- Earning a good brand name which will be an aid to internal customers.

In general, the Zero Defects Programme, if properly implemented, will produce improved results on a long-term basis to a manufacturing enterprise [20, 21].

### **9.13 Reliability of the Quality of Rubber-coated Textile Products**

To ensure the reliability of rubber-textile composites, testing of all the ingredients used in a rubber compound and the basic textile to find out about their purity and

performance should be carried out. Testing is essential if a rubber compound is prepared in addition to the utility of the basic textile used for reinforcement. From accuracy in weighing of compounding constituents to finished product testing, all tasks should meet the Six Sigma quality level to pass all the specified tests in assuring their performance and durability. Similarly, examination of the nature of composition of the textile, number of threads on warp and weft directions, type of weave of the fabric, weight per square metre, as well as measurement of breaking strength and tear strength will ensure final product performances and their suitability to a particular application.

The essential tests to abide by in the established standards for process quality checks during calendering or spreading while coating are: (i) coating thickness; (ii) width of fabric before and after coating; (iii) weight per square metre before and after coating; and (iv) adhesion strength.

Proceeding to the coating operation, the processes controlling measurement within tolerable limits are:

- Operating temperature of the mixing mill/internal mixture,
- Temperature at dumping,
- Storage temperature, condition and duration,
- Warm-up mill temperature,
- Processing temperature of bowls in the calendering machine, and
- Vulcanisation temperature, duration and platen pressure (if cured in presses).

The established test is the ‘ageing test’ after curing of rubber compounds utilised for coating. This will assist in ascertaining the effect of degradation by oxidation in the presence of atmospheric oxygen and surface cracking by traces of ozone which diminishes the life expectancy of the material. Ageing involves gradual changes in performance with time, the most serious effect is cracking on the surface, which reduces the life of the rubber coating [22].

### **9.13.1 Lifecycle Estimation of Coated Products**

Elastomeric-coated textile materials are widely used in industrial and engineering applications as well as in domestic situations. Increasing demands are placed on the products to withstand hostile conditions during service in outdoor applications. This

can involve direct sunlight and rain, use on abrasive surfaces, use at high atmospheric temperature, and also in corrosive environments such as saline water, acid, and alkalis.

These kind of conditions make the rubber-made product a highly challenging task for the manufacturer to estimate predictable service life to ensure better design of the product to assure their long-term functioning.

Measurement of fatigue, rupture in rubber surfaces and the textile used as the reinforcing member, and how this knowledge can be employed to predict and prolong the product's functional service life by determination of ageing performance, is important. The strength and weaknesses of such service prediction systems should also be considered. One should concentrate on analysing and improving the design and service life of the rubber fabric-coated products in domestic applications (rainwear, footwear, sheetings) as well as technical and engineering products (e.g., rubber boats, fuel tanks, floating bridges, rubber dams, conveyor belts, hoses) in which the rubber/textile functions as a composite.

The requirements of quality affirmation of the product are:

- Testing and development
- Testing of incoming basic materials such as rubber, chemicals and textiles
- On process testing
- Finished product testing
- Final inspection before dispatch
- Inspection of packaging

### ***9.13.2 Lifetime Prediction Techniques for Rubber-coated Fabrics***

The lifetime prediction techniques for rubber-coated fabrics are:

- Designing a relevant degradation process device for testing the made-up article.
- Setting up the apparatus and service condition resembling the actual use for in-house testing.
- Conduct standard accelerated ageing tests at different temperatures and durations for life estimation. Temperature range may be selected from 70 °C to 150 °C or higher depending upon the type of elastomer used. The duration of test should be 24-168 hours.



- Measurements of the rate of degradation at a higher temperature than the actual service temperature and at adverse atmospheric condition to predict the life of the item.
- Correlation of findings on actual field trials of the product which may be time-consuming but will confirm appraisal of the performance of the product and scope for its improvement.
- Maximum burst strength testing of made-up articles' representative sample (essentially for inflatable articles).

### ***9.13.3 Major Occurrences of Failure of Elastomer-coated Fabrics While Conducting Tests in the Laboratory***

Tests used in the laboratory include:

- Permeability of water/liquid.
- Permeability of air/gas.
- Swelling upon solvent contact.
- Cracking on surface due to flexing.
- Adhesion failure.
- Leaking/percolation of water/air/oil/gas from the seams in made-up articles.

### ***9.13.4 Probable Reasons for the Failure of Rubber-coated Products***

Probable reasons for the failure of rubber-coated products can be due to:

- Improper compounding ingredients for coating.
- Inappropriate selection of textiles.
- Incorrect design of the final product.
- Imperfect manufacturing system.
- Improper storage.
- Faulty installation of the item.

- Unforeseen service conditions.
- Unintentional mishandling.

The effects attributable to service life of rubber-coated items are:

- High temperature and harsh environment.
- Inconsistent static or dynamic loads, unwarranted stress or strain.
- In contact with oils and greases/chemicals during service (when a proper elastomer is not used).

To move towards ‘life assessment’:

- Identify the prevalent deteriorating processes.
- Set-up a similar service condition device at the laboratory scale and carry out accelerated ageing tests.
- Measure failure rates at higher temperature and extrapolate to the service temperature to determine the lifetime.
- Substantiate the findings from actual field trials.

As possibilities of failure of some rubber-coated products are concerned, they can be:

- Change in stiffness of the rubber coating for rainwear and other domestic products.
- Loss of rubber fabric adhesion strength such as canvas footwear, rubber-coated technical articles.
- Loss of adhesion strength on the seams of rubber-coated fabric articles (e.g., inflatable items).
- Deterioration by excessive swelling when in contact with oils or other fluids (e.g., hoses, canvas belts, fuel tanks)

#### **9.13.5 Selection of Tests in Life Prediction for Rubber-coated Textile Products**

The maximum life expectancy of a product fabricated out of elastomer-coated textiles under the conditions of use is naturally the first concern to the consumer. This demands a rubber-coated fabric material with good resistance to what is usually referred to as ‘ageing and weathering’ as well as resistance to any other harmful effect

that the article may encounter (e.g., oxygen, ozone, water, sunlight, oils, saline, acids, alkalis, excessive heat). In some uses, a prerequisite will be resistance to abrasion and endurance to stretching under static or dynamic stress/strain. Maximum resistance to tearing is also a demanding criterion for engineering applications. Many rubber-coated products are required to be in bright colours with a glossy finish for domestic and technical applications [22].

To maintain these properties in rubber-coated textile products throughout their predicted lifecycle is a major challenge for the manufacturer.

Scrutiny of the tests starting from the checking of raw materials on processed rubber compounds and the finished products will help to estimate the life expectancy of an article made out of an elastomer-coated textile.

The physical tests given next can impart an idea of performance characteristics of the finished product during its lifecycle:

- (1) Hardness – a lower hardness of the rubber coating compound will provide adequate flexibility/pliability to the coated material. Higher hardness will affect this property.
- (2) Tensile strength – rubber-coated textiles may be subjected to deforming forces such as extension, compression and thrust.

Moderate tensile strength gives an idea of the quality of the rubber compound used for coating; a high tensile strength of a rubber-coated compound is not very significant.

*Measurement of breaking strength* – it is a usual test to check the breaking strength of the raw fabric before rubber coating to judge its suitability for a particular finished product. The breaking strength of the coated material is also tested when preparing standard test pieces of 5 cm width ' 12 cm length to be used for the determination of physical strength resembling the functioning of the made-up item during service. A higher strength is necessary, particularly for technical and engineering application of rubber-coated textiles to withstand high impact strength (e.g., fuel tanks, rubber boats, floating bridges, rubber dams, beltings, pneumatic dock fenders).

Similarly, in domestic uses of rubber-coated fabrics, a specific strength is important to maintain proper performance during service (e.g., rainwear, footwear uppers, hospital sheeting, aprons).

- (3) Modulus is the load required to stretch a vulcanised rubber to a stated elongation. This is the measurement of stiffness of the rubber compound used for coating.

In some applications (e.g., air pillows, airbeds, waterbeds) low modulus rubber compounds are necessary for rubber coating the fabric to maintain the flexibility of the products.

- (4) Abrasion – moderately high abrasion resistance is desirable if the elastomer-coated fabric is used on abrasive surfaces (e.g., helicopter landing gear, landing pads, collapsible fuel tanks, waterproof covers, tarpaulins).
- (5) Tear resistance is an imperative test for elastomer-coated textile materials. This is the resistance to the growth of a cut if tension is applied to the cut while the rubber-coated textile items are in service. High tear strength is specifically important to rubberised canvas uppers industrial boots, floating bridges, rubber dams, textile-reinforced rubber hoses, and rubber-coated textile tarpaulins.
- (6) Adhesion strength – specific rubber/textile adhesion is primarily important for effective performance of the items produced from rubber-textile composites.

High adhesion strength is a requirement for industrial/engineering uses of coated textiles. Measurement of adhesion strength in the laboratory before ageing and after accelerated ageing at different temperatures to determine the probable deteriorating effect during the service of the composite material is necessary. The adhesion strength is affected while the coated product is in high flexing zone or in use in an aggressive atmosphere. Contact with oil in service also has a weakening effect on adhesion strength, which compromises service performance.

Specifically, high adhesion strength is essential at the seams/joints on fabricated articles made from rubber-coated textiles, particularly for inflatable items. Seam strength can be measured on test pieces prepared from rubber-coated textile strips of 50 mm width  $\times$  250 mm length. Two pieces of coated material are adhered together with rubber adhesive on their coated surfaces using self-cured rubber-based adhesive or they can be suitably vulcanised using heat curable cement. Tests may be carried out in an apparatus suitable for a ply separation test using the dead load method or in a tensile testing machine to measure the seam strength following the test method BS903: Part 31 [23].

- (7) Flex-cracking and fatigue resistance: cracks appear on the surface of the rubber coating if a rubber-coated textile product is subjected to continuous flexing on exposure to atmospheric oxygen. Formation and subsequent growth of such cracks ultimately leads to failure of the item. A resilient coating uses up most of the energy expended in deforming it, and in returning it back to shape.

Rubber coatings with high resiliency generate less heat because of the lower amount of energy available for heat generation. High heat generation may shorten the life of the coated product. Thus, higher-resilient coating materials provide

a longer life. The tests can be conducted on a rubber flexing machine using test pieces prepared from the same rubber compound utilised for coating or in a specially designed rig to test coated samples BS903: Part 26 [23].

- (8) Ageing and weathering - there are various deteriorating effects which have a vital role in the ageing and weathering of rubber coating.

Accelerated ageing tests, if conducted in a laboratory on test pieces, give substantial information about the expected service life of the end product, BS 903: Part 13 [23].

Depending on the criticality of use of the end product, the test temperature may vary from 70 °C to 150 °C, and the duration of test may range from 24 hours to 30 days until a 50% change in property is observed in the test sample.

Ozone is present in the atmosphere in varying small concentrations. It has a destructive effect on rubber if it is not protected with anti-ozonants while compounding. Tests can be conducted in the laboratory using representative test pieces at different concentrations of ozone to evaluate the effect of ozone on the coating surfaces.

For the purpose of general weather resistance tests, samples of rubber-coated products in stretched or unstretched condition are often exposed outdoors. Ultraviolet lamps may be used in the laboratory to examine colour fading, specifically for coloured rubber-coated materials. This can also be tested exposing a sample of coated fabric to direct sunlight.

Exposure to artificial rain can also be arranged to check the water penetration, especially for the rainwear seams and other fabricated items where the joints have to be waterproof.

- (9) Chemical/solvent resistance - a functional test for chemical resistance involves immersing a small piece of rubber-coated material in the liquid/solvent under investigation.

The concentration, temperature and immersion period should be controlled and the resulting changes in volume or any deteriorating effect examined and noted.

- (10) Biological degradation – microbiological deteriorations have an effect on rubber-coated material used outdoors. This is caused by attack of micro-organisms or different species of fungus.

This kind of problem occurs in natural rubber-coated cotton fabric but to a lesser extent in synthetic rubber-coated textile products. The situation is particularly

significant in tropical regions, and is particularly damaging in dark and damp environments [24].

Infection with micro-organisms may reduce the physical properties of the coated products, and exposure for a longer period in such environments will ultimately degrade the material. Such circumstances may also destroy the appearance of coloured rubber coatings.

A simple test can be conducted on small pieces of rubber-coated fabrics buried in soils in a similar atmosphere. After a period of time the test pieces can be taken out, tested visually and physically to observe deterioration from the original properties.

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# Abbreviations

2D	Two-dimensional
3D	Three-dimensional
6PPD	Phenyl- <i>p</i> -phenylenediamine
AA	Acrylic acid
AATCC	American Association of Textile Chemists and Colorists
ACN	Acrylonitrile
AlCl <sub>3</sub>	Aluminium chloride
ANN	Artificial neural network
ASTM	American Society for Testing and Materials
BIIR	Bromobutyl rubber(s)
BIS	Bureau of Indian Standards
BR	Butyl rubber
BS	British Standard
BTT	Breakthrough time
CBS	Cyclohexylbenzothiazolesulfenamide
CI	Coumarone-indene
CNT	Carbon nanotubes
CO <sub>2</sub>	Carbon dioxide



COSHH	Control of Substances Hazardous to Health
CR	Chloroprene rubber
CSM	Chlorosulfonated polyethylene
CV	Constant viscosity
CWA	Chemical warfare agent
DBP	Dibutyl phthalate
DCPD	Dicyclopentadiene monomer
DEA	Dielectric elastomer actuator
DEG	Diethylene glycol
DPG	Diphenyl guanidine
DPNR	Deproteinised natural rubber
DPPD	Diphenyl- <i>p</i> -phenylene-diamine
DT	Double texture
DTex	Decitex
EAP	Electroactive polymers
EC	European community
EMI	Electromagnetic interference
ENB	Ethylidene norbornene monomer
ENR	Epoxidised natural rubber
EPDM	Ethylene-propylene-diene terpolymer
EPM	Ethylene propylene rubber
FA	Formic acid
FC	Fluorocarbon

FDA	Food and Drug Administration
FEF	Fast extrusion furnace carbon black
FR	Flame retardancy
GC-FPD	Gas chromatography–flame photometry detection
GC/FID	Gas chromatography–flame ionisation detection
GPF	General Purpose Furnace
H <sub>2</sub> O	Water
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
HCl	Hydrogen chloride
HD	Common term for sulfur mustard (a type of chemical warfare agent)
HDPE	High-density polyethylene
HIV	Human immunodeficiency virus
HMMM	Hexamethoxymethyl melamine
HMT	Hexamethalene tetramine
HNBR	Hydrogenated nitrile rubber
HNBR	Hydrogenated nitrile rubber
HSR	High Styrene resins
HWM	High wet modulus
IARC	International Agency for Research on Cancer
IIR	Isobutylene-isoprene rubber
IR	Infrared
IS	Indian Standard
ISO	International Organization for Standardization

KOH	Potassium hydroxide
LDPE	Low-density polyethylene
LOI	Limited/Limiting Oxygen Index
MBT	Mercaptobenzthiazole
MBTS	Dibenzthiazyl disulfide
Mc	Network chain molecular weight
MG	Methacrylate graft rubbers
MMA	Methylmethacrylate
MPCM	Microencapsulated Phase Change Material(s)
MVTR	Moisture vapour transmission rate
N <sub>2</sub> O	Nitrous oxide
NA	Avogadro's number
NATO	North Atlantic Treaty Organisation
NBC	Nuclear, biological and chemical warfare
NBR	Nitrile butadiene rubber
NDPA	Nitrosodiphenylamine
NDPA	Nitrosodiphenylamine
NO <sub>2</sub>	Nitrogen dioxide
NR	Natural rubber
OFT	Optical Fibre Technology
PA	Polyamide
PAN	Polyacrylonitrile
PBR	Polybutadiene Rubber

PC	Personal Computer
PCM	Phase Change Material(s)
PE	Polyethylene
PEG	Polyethylene glycol
PEN	Polyethylene naphthalate
PET	Polyethylene terephthalate
phr	Parts per hundred rubber
PMMA	Poly methyl methacrylate
PNIPAAm	Poly <i>N</i> -isopropyl acrylamide
PP	Polypropylene
pphm	Parts per hundred million
ppm	Parts per million
PPTA	Poly(paraphenylene terephthalamide)
PRI	Plasticity retention index
PT	Polythiophenes
PTFE	Polytetrafluoroethylene
PU	Polyurethane(s)
PVA	Polyvinyl acetate
PVAc	Polyvinyl acetate
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
QC	Quality control
QMS	Quality management system

RF	Resorcinol formaldehyde
RFI	Radio-frequency interference
RFL	Resorcinol-formaldehyde-latex
RH	Relative humidity
RIB	Rigid-hulled inflatable boats
rpm	Revolutions per minute
RSS	Ribbed Smoked Sheet
SBR	Styrene-butadiene rubber
SiO <sub>2</sub>	Silicon dioxide
SMP	Shape memory polymers
SMPU	Segmented polyurethane
SMR	Standard Malaysian Rubber
SnCl <sub>2</sub>	Tin chloride
SO <sub>2</sub>	Sulfur dioxide 7
SP	Superior processing natural rubber
SPC	Statistical Process Control
SRF	Semi-reinforcing carbon black
SSP	Stimuli-sensitive polymer(s)
ST	Textiles coated on one surface
TAP	Threshold ageing process
T <sub>C</sub>	Temperature for a constant decomposition level
TFP	Tailored fibre placement
T <sub>g</sub>	Glass transition temperature

TGA	Thermogravimetric analysis
T <sub>m</sub>	Melting temperature
TMQ	Polymerised trimethyl dihydroquinoline
TMQ	Polymerised dihydroquinoline
TMTD	Tetramethyl thiuram disulfide
TPU	Thermoplastic elastomers
TQC	Total quality control
TQM	Total quality management
UV	Ultraviolet
VDC	Vinylidene chloride monomer
VGC	Viscosity gravity constant
VP	Vinyl pyridine
XNBR	Carboxylated nitrile rubber
XNBR	Carboxylated nitrile rubber
ZDC	Zinc dithiocarbamates
ZOPP	Ziel-Orientierte Projekt Planung



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Published by Smithers Rapra Technology Ltd, 2012

Polymer coated textiles are known as engineered composite materials at macro scale. Coating can offer significant improvements to the substrate, thanks to a combination of physical (such as impermeability and fabric abrasion), chemical and aesthetic components. The number of polymer combinations enables a wide variety of textile substrate structures and new, innovative applications are being introduced almost every day.

The polymer coated textile industry runs in parallel with the developments in textile research: applications such as reactive coatings with nanoparticles (with self-cleaning, self-sterilising surfaces), systems with conductive polymer coatings to provide EM shielding, electronic textile systems (with body monitoring properties), environmental responsive systems and so forth, are already somewhat classical and are continually being developed and updated.

*Advances in Polymer Coated Textiles* is an up-to-date summary of the technical textile industry, considering the passage from conventional to emerging technologies. It discusses the criteria for selection of coating and textile and summarises the manufacturing basics of the system. It explores a range of emerging technologies, including smart, intelligent and nanostructured applications, alongside the testing and quality control methods of such systems.

This book is a must for textile and polymer technologists, engineers, scientists and students and all those who are interested in this interdisciplinary field.